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Interaction of hydrogen peroxide and chlorine dioxide stages in ECF bleaching

DAVID J. SENIOR, JANICE HAMILTON, ARTHUR J. RAGAUSKAS, JAMES SEALEY, AND PETER FROASS

ABSTRACT

Changing the order of the hydrogen peroxide (P) and chlorine dioxide (D) stages in an ECF (elemental chlorine free) bleach sequence was shown to affect the final brightness of kraft pulps. Application of a D(EOP)DPP bleach sequence to a southern softwood pulp produced consistently higher interstage and final brightnesses than a D(EOP)PDP sequence. These results were confirmed by bleaching a northern softwood and a eucalypt pulp using DEDP and DEPD sequences. In all cases, higher brightnesses were achieved when the second D stage (D_2) preceded the P stage. The effect was especially evident with the hardwood pulp, where brightness of the DEDP pulp was three points higher than the DEPD pulp. NMR analysis of extracted lignin showed that the D_2 stage reduced the phenolic lignin content of softwood pulp by 60%, while the P stage had no effect. For the hardwood pulp, the D_2 stage reduced the phenolic lignin content by 90–95%. The greater bleaching efficiency of a DEDP sequence (compared with DEPD) is consistent with known reactivities of hydrogen peroxide and chlorine dioxide toward specific lignin structures. The D_2 stage lowers the phenolic lignin content of pulp while generating hydrogen peroxide-sensitive, nonphenolic lignin species. A followup P stage reacts effectively with this lignin.

Application:

Explains why the second D stage should precede the first P stage in a kraft pulp bleaching sequence.

HYDROGEN PEROXIDE HAS BEEN used routinely in the bleaching of mechanical pulps for many years *(1)*. Now it is being used increasingly in kraft mills as an addition to extraction stages or as full P stages. Increasing the use of hydrogen peroxide in ECF (elemental chlorine free) bleaching has allowed mills to reduce their use of chlorine dioxide in both shortened *(2,3)* and full bleach sequences *(2,4, 5)*. There are many reasons why a mill might choose to reduce its chlorine dioxide consumption. It could be part of a strategy to overcome limitations in chlorine dioxide generating capacity, or it could be part of a program to optimize overall bleaching costs *(4,6,7)*. Some mills use hydrogen peroxide as a substitute for chlorine dioxide in an effort to reduce AOX (adsorbable organic halides) in ECF (elemental chlorine free) bleaching. Full-scale mill studies already indicate that extensive environmental gains can be made by moving to ECF bleaching *(8,9)*.

Earlier work by Gellerstedt and Pettersson *(10)* identified optimal conditions for the use of hydrogen peroxide as a pulp bleaching agent. These include strict control of transition-metal concentration in pulps *(11)* and stabilizing hydrogen peroxide so that it does not decompose to form cellulose-damaging free radicals *(5, 11–15)*. Another prerequisite to high-brightness bleaching with hydrogen peroxide is that the pulps be delignified as fully as possible prior to entering the bleach plant *(3, 16–18)*. Clearly, extended cooking and oxygen delignification play an important role in optimizing hydrogen peroxide use. The best conditions for hydrogen peroxide bleaching should typically include 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 using 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 *et al. (2)* demonstrated that the position of a hydrogen peroxide-reinforced extraction stage within a bleach sequence could affect chemical consumption, brightness, and AOX. Devenyns *et al. (5)* evaluated the use of hydrogen peroxide as a replacement for chlorine dioxide by applying it as either a prebleaching or final brightening stage. Similarly, Reeves *et al. (7)* discussed the impact of the position of a hydrogen peroxide (pressurized) stage on equipment layout and chemical consumption efficiency. The literature contains a tremendous volume of data about hydrogen peroxide bleaching, and studies such as those cited here reflect efforts to optimize its use. However, there is very little information regarding the impact of a hydrogen peroxide stage on the performance of a subsequent chlorine dioxide stage or vice versa.

An extensive evaluation by Malinen *et al. (6)* focused on minimizing the use of chlorine dioxide while bleaching pulps to high brightness.

D_1 STAGE				EOP STAGE [a]	P_1 STAGE [b]			D_2 STAGE [c]				P_2 STAGE [d]		
ClO_2 charge, % on pulp	Kappa factor	Exit pH	Residual, % on pulp	Brightness, % ISO	pH (in/out)	Residual, % on pulp	Brightness % ISO	ClO_2 charge, % on pulp	Exit pH	Residual, % on pulp	Brightness, % ISO	pH (in/out)	Residual, % on pulp	Brightness, % ISO
CONTROL PULPS														
1.59	0.15	2.4	…	50.0	10.7/10.3	0.14	60.6	0.6	3.7	…	78.0	10.6/9.6	0.03	81.6
								1.0	3.8	…	82.7	10.8/9.3	0.02	85.3
1.91	0.18	2.3	0.03	54.4	10.6/9.6	0.12	65.8	0.6	3.8	0.02	83.6	10.7/9.4	…	85.6
								1.0	3.2	0.03	86.0	10.7/9.1	0.035	87.8
2.12	0.20	2.3	0.04	54.1	10.6/10.1	0.14	67.8	0.6	3.7	0.03	82.7	10.5/9.3	0.12	85.8
								1.0	3.3	0.05	86.7	10.8/9.2	0.03	87.8
XYLANASE-TREATED PULPS														
1.56	0.15	2.4	…	51.0	10.6/10.2	0.22	61.7	0.6	3.6	…	79.2	10.8/9.7	0.02	82.7
								1.0	3.2	0.01	83.6	10.8/9.4	0.025	86.5
1.88	0.18	2.4	0.05	55.5	10.7/9.8	0.12	67.1	0.6	3.8	0.06	84.1	10.8/9.7	…	86.4
								1.0	3.3	0.08	86.6	11.0/9.3	0.035	88.9
2.08	0.20	2.3	0.06	55.7	10.7/10.4	0.17	68.3	0.6	3.7	0.13	83.5	10.7/9.6	0.11	86.4
								1.0	3.3	0.15	86.9	10.9/9.4	0.03	89.2

[a] 2.8% NaOH, 0.4% H_2O_2 (o.d. pulp basis)
[b] 1% H_2O_2, 0.05% $MgSO_4$, 0.45% NaOH (o.d. pulp basis)
[c] 0.1% NaOH (o.d. pulp basis)
[d] 0.5% H_2O_2, 0.35% NaOH (o.d. pulp basis)

I. D(EOP)PDP bleaching of southern softwood kraft pulp

Closer reexamination 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 was also higher.

An ECF bleaching evaluation was conducted in our laboratory on a southern softwood pulp using the sequence D(EOP)PDP. [The two chlorine dioxide (D) and hydrogen peroxide (P) stages are numbered in the discussion as D_1 (EOP) P_1 D_2 P_2.] When the sequence order was reversed to D(EOP)DPP, an increase in brightness was consistently observed. These results were consistent with the work of Malinen *et al. (6)* and suggested that the order of the D_2 and P stages might influence each other by either chemical or physicochemical means. When this work was repeated on other hardwood and softwood pulps, the same effect was seen.

The data presented in the current work demonstrate that the bleaching performance of chlorine dioxide and hydrogen peroxide is affected by their sequence of addition. This phenomenon is discussed with regard to the changing structure of lignin during bleaching and the reactivity of chlorine dioxide and hydrogen peroxide to the different types of lignin.

EXPERIMENTAL

Bleaching experiments were carried out on brownstock softwood and hardwood pulps. Two softwood pulp samples were studied: The first was a southern U.S. softwood (kappa no. 28.0), and the second was an eastern Canadian softwood (kappa no. 26.6). The hardwood sample was a South American eucalypt (kappa no. 12.4).

Large 300-g batches were prepared for lignin extraction and analysis; smaller (30 g or 20 g) samples were used for the bleaching runs. Chemical charges are expressed as percent on ovendry (o.d.) 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 sulfuric acid to a pH of 2 in the 1% consistency wash.

Chlorine dioxide (D)

Elemental-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.

D_1 stages were carried out at 3.5% consistency and 50°C for 30 min. 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 of the hardwood.

D_2 stages were carried out at 6% consistency and 80°C for 180 min. 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, while two charges of 0.6% and 1.0% were used on the southern U.S. pulps.

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.

D_1 STAGE				EOP STAGE [a]	D_2 STAGE				P_1 STAGE [b]			P_2 STAGE [c]		
ClO_2 charge, % on pulp	Kappa factor	Exit pH	Residual, % on pulp	Brightness, % ISO	ClO_2 charge, % on pulp	Exit pH	Residual, % ISO	Brightness pulp	pH (in/out)	Residual, % on pulp	Brightness, % ISO	pH (in/out)	Residual, % on pulp	Brightness, % ISO
CONTROL PULPS														
1.59	0.15	2.4	…	50.0	0.6 [d]	3.7	…	73.5	10.5/9.4	0.07	82.4	10.7/10.2	0.01	82.8
					1.0 [e]	3.7	…	77.6	10.4/9.5	0.08	85.9	10.8/10.3	0.01	85.6
1.91	0.18	2.3	0.03	54.4	0.6 [d]	4.0	0.04	78.8	10.4/10.0	0.04	85.1	10.8/10.2	0.02	85.2
					1.0 [e]	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	2.3	0.04	54.1	0.6 [d]	3.5	0.02	79.3	10.5/9.7	0.11	86.1	10.7/10.0	0.03	86.8
					1.0 [e]	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	2.4	…	51.0	0.6 [d]	3.6	0.01	73.8	10.5/9.8	0.18	83.2	10.8/10.3	0.01	83.7
					1.0 [e]	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	2.4	0.05	55.5	0.6 [d]	3.2	0.05	80.0	10.4/10.2	0.05	86.9	10.9/10.3	…	87.4
					1.0 [e]	3.4	0.07	83.0	10.5/10.3	0.25	88.6	10.9/10.3	…	88.8
2.08	0.20	2.3	0.06	55.7	0.6 [d]	3.7	0.04	80.7	10.4/10.0	0.06	87.1	10.8/10.3	0.02	88.0
					1.0 [e]	3.4	0.19	83.3	10.4/9.9	0.12	88.6	10.7/10.2	0.02	89.3

[a] 2.8% NaOH, 0.4% H_2O_2 (o.d. pulp basis)
[b] 1% H_2O_2, 0.05% $MgSO_4$, 0.45% NaOH (o.d. pulp basis)
[c] 0.5% H_2O_2, 0.35% NaOH (o.d. pulp basis)
[d] 0.1% NaOH on o.d. pulp
[e] 0.2% NaOH on o.d. pulp

II. D(EOP)DPP bleaching of southern softwood kraft pulp

Caustic extraction (E)

Extractions were performed on 150-g or 20-g lots (as required) by adding caustic soda and the required amount of water to the pulp 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 min. 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 (P)

Charges of 1.0% and 0.5% were applied in the two P stages, respectively, for 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. The P stages were carried out at 12% consistency and 80°C for 120 min. Magnesium sulfate was included at 0.05% (on o.d. 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 ovendry weight of pulp. Brightnesses—reported as percent ISO brightness—were measured using a Zeiss Elrepho photoelectric reflectance photometer on 4-g (o.d.) sheets.

Procedure for isolating residual lignin

Residual lignins were isolated by mild acid hydrolysis as described by Gellerstedt *(24)*. Slight modifications to Gellerstedt's procedure were made. The complete procedure is 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 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, washed with distilled water three times, and then freeze-dried. The average yield was 40% (based on kappa numbers).

^{31}P NMR analysis of residual lignin

Residual lignin characterization was performed by ^{31}P NMR (nuclear magnetic resonance) analysis as described by Argyropoulos *(25)*. The phosphitylation reagent used in this quantitative analysis was 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane. Two stock solutions were prepared. The first was a solution of pyridine and deuterated chloroform in a 1.6/1 v/v (volume per volume) 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

D_1E STAGES [a]				P STAGE [b]		D_2 STAGE [c]	
D_1 exit pH	pH (in/out)	Kappa number	Brightness, % ISO	pH (in/out)	Brightness, % ISO	Exit pH	Brightness, % ISO
DEPD SEQUENCE							
2.4	11.2/11.1	9.4	43.2	10.7/9.8	64.8	3.2	83.8
DEAPD SEQUENCE							
2.6	11.2/11.0	9.4	46.1	10.9/10.0	66.5	2.9	83.9
DEPAD SEQUENCE							
2.6	11.2/11.0	9.4	46.1	11.2/10.4	65.2	2.9	84.6
DEDP SEQUENCE							
				D_2 STAGE [c]		P STAGE [b]	
				Exit pH	Brightness, % ISO	pH (in/out)	Brightness, % ISO
2.4	11.2/11.1	9.4	43.2	3.4	72.4	10.8/10.0	84.7

[a] 1.82% ClO_2, 2.5% NaOH
[b] 2% H_2O_2, 0.05% $MgSO_4$, 0.8% NaOH
[c] 1.2% ClO_2, 0.3% NaOH

III. DEPD and DEDP bleaching of northern softwood kraft pulp

D_1E STAGES [a]				P STAGE [b]		D_2 STAGE [c]	
D_1 exit pH	pH (in/out)	Kappa number	Brightness, % ISO	pH (in/out)	Brightness, % ISO	Exit pH	Brightness, % ISO
DEPD SEQUENCE							
3.2	11.0/10.9	7.7	55.6	10.8/10.0	70.3	3.9	84.2
DEAPD SEQUENCE							
2.8	11.0/10.6	7.7	57.0	10.7/9.9	69.6	2.7	83.0
DEPAD SEQUENCE							
2.8	11.0/10.6	7.7	56.1	11.0/10.2	71.2	2.5	84.0
DEDP SEQUENCE							
				D_2 STAGE [c]		P STAGE [b]	
				Exit pH	Brightness, % ISO	pH (in/out)	Brightness, % ISO
2.9	11.2/11.1	7.7	55.8	3.9	80.3	11.0/10.6	87.6

[a] 0.47% ClO_2, 2.2% NaOH
[b] 2% H_2O_2, 0.05% $MgSO_4$, 0.9% NaOH
[c] 1.2% ClO_2, 0.1% NaOH

IV. DEPD and DEDP bleaching of hardwood kraft pulp

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 the solution was allowed to stir for 2 min before being transferred into an NMR tube and tested. NMR analysis was performed on a Bruker 400 DMX with a 25-s 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.

Pulp	Manganese, ppm	Iron, ppm
Softwood*		
Brownstock	114.4 ± 2.40	50.76 ± 0.39
DE	9.85 ± 1.11	49.80 ± 0.64
DEA	3.78 ± 0.81	40.26 ± 1.47
Hardwood		
Brownstock	30.08 ± 0.05	43.00 ± 2.29
DE	1.85 ± 0.04	47.98 ± 8.88
DEA	0.51 ± 0.09	38.77 ± 4.42

*Northern softwood

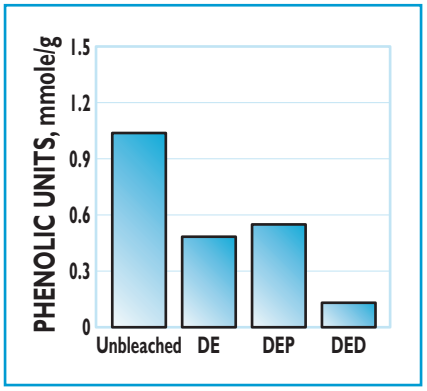
V. Manganese and iron in acid-washed pulps

RESULTS AND DISCUSSION

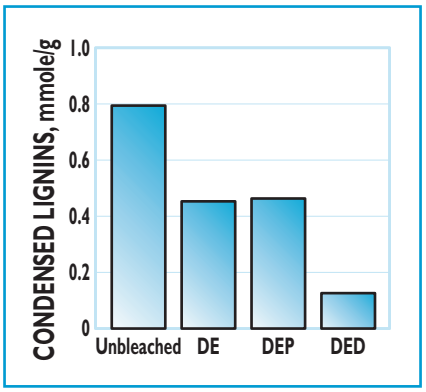
During the course of ECF bleaching of a softwood kraft pulp from a southern U.S. mill, it was observed that the order of hydrogen peroxide (P) and chlorine dioxide (D_2) stages consistently affected the brightness of the pulps. Specifically, when the D_2 stage was placed before the P stage, the brightness of the pulp was higher. The work was extended to another softwood and a hardwood pulp to confirm the observation.

The initial objective of the bleaching study using the southern softwood pulp was to identify the final brightnesses obtained using several different ECF sequences. The particular mill producing the pulp was converting from the use of chlorine and hypochlorite in its bleach sequence to an ECF sequence. They were investigating the potential of using the redundant hypochlorite tower as a P-stage tower. The chemical charges and bleaching conditions were provided by the mill.

Table I shows the various interstage and final brightnesses for the sequence D(EOP)PDP. Using this sequence, the highest kappa factor applied in the D_1 stage resulted in a final brightness of 87.8% ISO. The same pulp was pretreated with xylanase enzyme to determine if the brightness ceiling could be increased. When this pulp was pre-



1. Phenolic content of northern softwood pulp



2. Condensed lignin content of northern softwood pulp

treated with xylanase (Ecopulp® X-200), an additional point in brightness was reached (89.2% ISO), which indicated that a further gain in brightness was possible. Similar gains were also seen at each of the lower kappa factors. The brightness gains obtained with the enzyme pretreatment suggested that the pulp had hit a brightness ceiling with the D(EOP)PDP sequence. When the bleaching was repeated in a D(EOP)DPP sequence (i.e., with the position of the P_1 and D_2 stages reversed), the final brightnesses also increased in general by a point, as seen in **Table II**.

A comparison of the brightnesses for the D(EOP)PDP and D(EOP)DPP sequences before the second P stage (i.e., D(EOP)PD and D(EOP)DP brightnesses) 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. Under these conditions, the final brightness of the southern softwood pulp was clearly higher when the D_2 stage preceded the P_1 stage.

This comparison was then applied to a northern softwood pulp to see if the order of D_2 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 that was about one brightness point higher than the DEPD sequence, as seen in **Table III**. A hardwood (eucalypt) kraft pulp was also bleached using the same sequences. In this case, the difference in brightness using the DEDP sequence was a full three brightness points higher than the DEPD sequence, as seen in **Table IV**. Clearly, the placement of the D_2 stage before the P_1 stage produced higher brightnesses for both hardwood and softwood pulps.

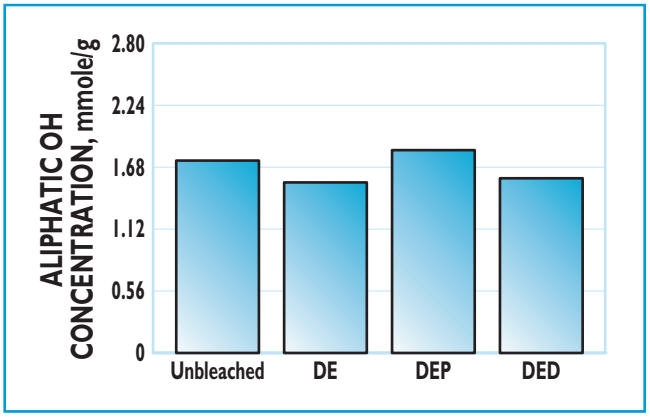
It was immediately assumed that the higher final brightness of the DEDP pulp over the DEPD pulp could be attributed to the improved P-stage performance because of the removal of metals in the D_2 stage. Presumably, this would be a result of the acidic wash effect of the D_2 stage. An economical way of performing a mild acid wash to reduce transition metals is to employ a chlorine dioxide stage prior to the P stage *(2, 5)* or an acidic filtrate wash *(20)*.

To determine if the levels of metals might play a role in the performance of the P stage, metals levels were measured for the northern softwood and hardwood pulps in the brownstock, after the DE stages, and after a dedicated acid wash (DEA stages). As seen in **Table V**, the manganese level of the softwood brownstock was quite high (114 ppm), but it was lowered to 10 ppm by the acidic effect of the first bleach (D_1) 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 ppm and 0.5 ppm, respectively. The iron content of either pulp was only slightly affected by acidic treatments.

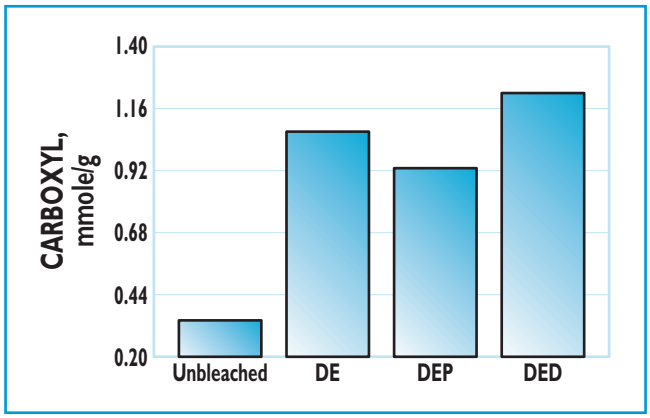
The improved performance of the peroxide stage following the acid wash (DEAPD) sequence can be seen by comparing the P-stage brightnesses in Table III. Reducing the manganese level from 10 ppm to 4 ppm permitted a brightness gain of more than 1.5 ISO points. However, this gain was not passed to the post-D_2 brightness to any significant extent. Conversely, the acid wash placed before the D_2 stage (DEPAD) gave a slight increase in brightness.

An explanation for the difference in final brightness of the DEPD and DEDP pulps relates to the order of addition of the D_2 and P stages (PD vs. DP). Changes in lignin structure during bleaching likely affect the reactivity of the bleaching agent applied in the subsequent stage. In the case of the DEDP sequence, the D_2 stage produces a lignin that is sensitive to reaction with hydrogen peroxide in the following P stage, thus resulting in the higher final brightness. Conversely, in the case of the DEPD sequence, the P stage does not increase the sensitivity of the lignin to reaction with the chlorine dioxide. Thus the P stage placed before the D_2 stage has a minimal effect on improving the chemistry of the chlorine dioxide in the D_2 stage.

To determine if there could be a chemical basis for the difference in bleaching response of DEDP and DEPD pulps, the lignin content at various stages in the bleaching process was analyzed by ^{31}P NMR. This



3. Aliphatic hydroxyl content of northern softwood pulp



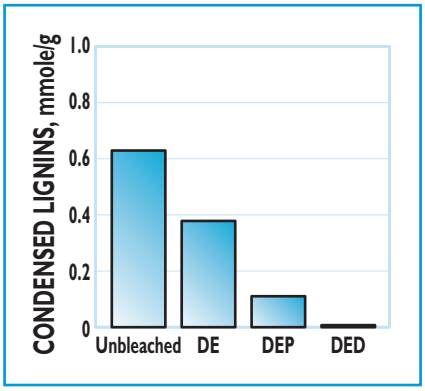
4. Carboxyl content of northern softwood pulp

technique was recently developed by Sun and Argyropoulos *(26)* to investigate the mechanism of oxygen or EOP delignification by studying the changes in lignin structure during each process.

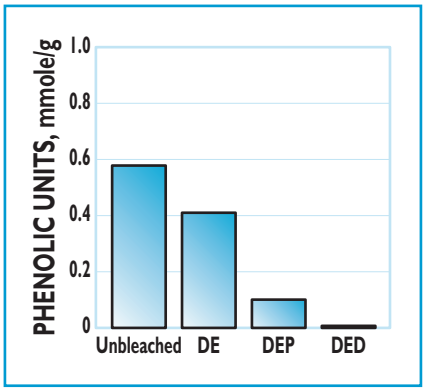
Lignin was extracted from unbleached, DE-, DEP-, and DED-bleached softwood and hardwood pulps. Extracted lignin was then prepared for ^{31}P NMR analysis. The most notable differences were in the contents of phenolic and condensed lignins for both the softwood and hardwood pulps.

The phenolic and lignin contents of the northern softwood pulps after various bleaching stages are depicted in **Figs. 1 and 2**, respectively. The DEP- and DE-treated pulps are virtually identical in both figures, indicating that the peroxide treatment had no effect on either species. However, both species were reduced by about 60–70% after the D_2 stage (DED pulp). Thus, in the case of a DEPD sequence, the D_2 stage is acting on a DEP pulp that has the same phenolic lignin content as a DE pulp.

Under the practical conditions of bleaching, chlorine dioxide reacts mainly with phenolic hydroxyl lignin *(27)*. Clearly, in the case of the DEPD pulp, the hydrogen peroxide stage has done very little to remove the target substrate of the D_2 stage, resulting in lower brightness. On the other hand, the D_2 stage of the DED sequence removed 60–70% of the phenolic lignin from the pulp.



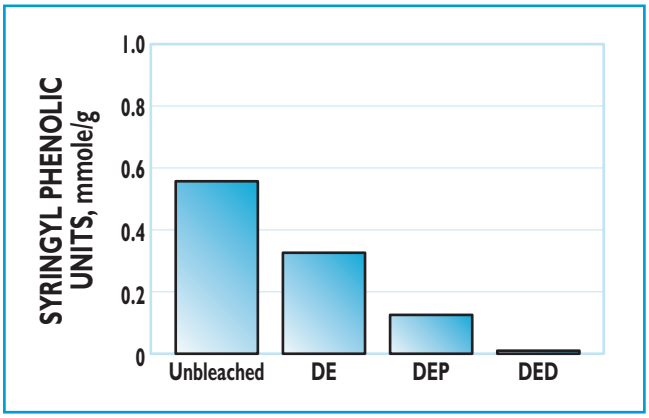
5. Condensed lignin content of hardwood pulp



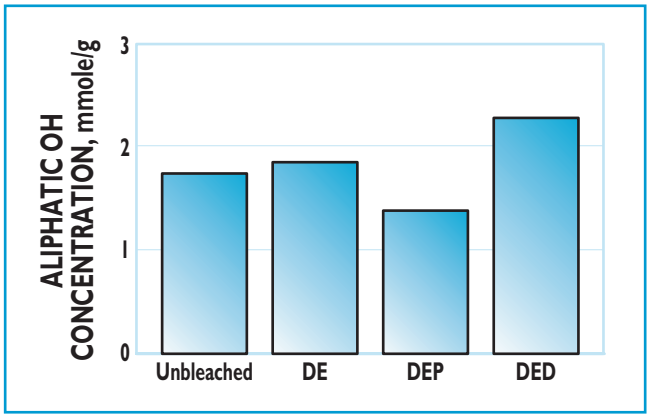
6. Guaiacyl and demethylated phenolic content of hardwood pulp

The products of chlorine dioxide treatments include various quinones and other conjugated chromophores *(27–32)*. Although some of these are removed by various degradation products of chlorine dioxide—such as chlorine, chlorous acid, and hypochlorous acid—many of the products of the D_2 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 *(28)*, rather than aromatic structures. Therefore, for the DEDP sequence, the D_2 stage acts to bleach and remove lignin, and in doing so, it prepares the pulp for subsequent treatment by hydrogen peroxide. Thus it is not surprising that the DEDP pulp is brighter than the DEPD pulp. [Note that formation of free radicals (HO_2) does occur with hydrogen peroxide, and these free radicals can attack the aromatic groups in lignin *(33)*. However, reaction conditions (pH, metal levels, magnesium-to-manganese ratio) are optimized to minimize the formation of free radicals, which indiscriminately attack both lignin and cellulose, thus leading to strength loss.] **Figures 3 and 4** show the aliphatic hydroxyl and carboxyl concentrations, respectively, for the softwood pulp after various stages of bleaching.

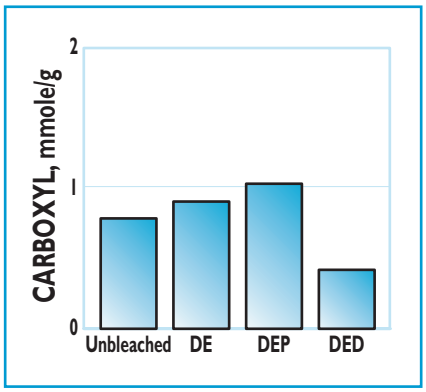
The difference between the brightness of the DEPD and DEDP softwood pulps was even greater for the hardwood pulp. Analysis of the hardwood lignin by ^{31}P NMR supports this difference. Similar to the softwood pulp, treatment of DE hardwood pulp with chlorine dioxide (D_2) significantly reduced the lignin



7. Syringyl phenolic content of hardwood pulp



8. Aliphatic hydroxyl content of hardwood pulp



9. Carboxylic acid concentration of hardwood pulp

content. The concentration of condensed lignins (**Fig. 5**) and phenolic content (**Fig. 6**, guaiacyl and demethylated phenolics; **Fig. 7**, syringyl phenolics) were reduced by 90–95%, compared with about 60–70% for the softwood pulp. Unlike the softwoods, however, treatment of the hardwood DE pulp with hydrogen peroxide removed more than 50% of the phenolic and lignin content.

Another difference between hardwood and softwood bleached pulps was that hydrogen peroxide treatment reduced the aliphatic hydroxyl content of hardwood DE pulp, whereas chlorine dioxide treatment increased it, as seen in **Fig. 8**. Essentially, no change was seen in the softwood experiments (Fig. 3).

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, as seen in **Fig. 9**. The softwood pulp showed very little difference (Fig. 4).

A review of the mechanisms of pulp bleaching by hydrogen peroxide and chlorine dioxide reveals that each agent is most effective acting on specific structures. Chlorine dioxide strongly attacks phenolic hydroxyl lignin species, whereas hydrogen peroxide preferentially attacks carbonyl and conjugated carbonyl 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 D_2 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 the lignin in the DE pulp. The subsequent D_2 stage must then act on a DEP pulp that is essentially identical to a DE pulp. This explains the reduced brightness obtained with a DEPD sequence.

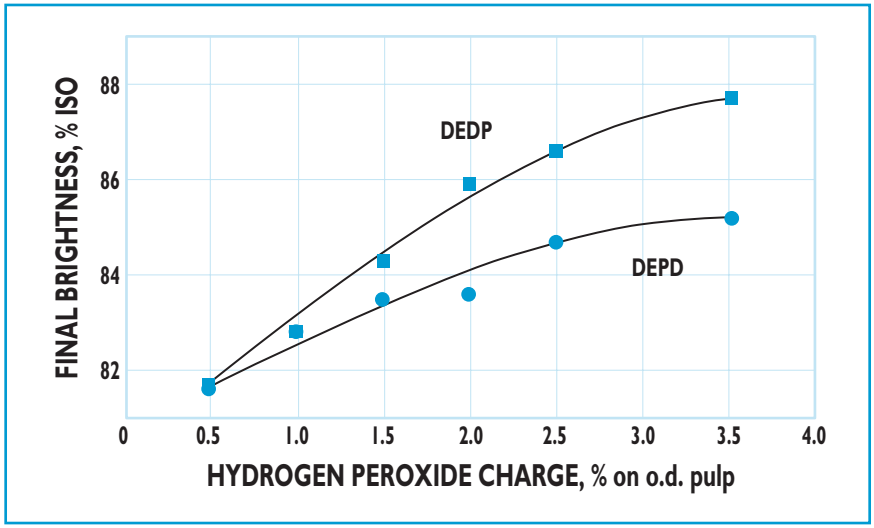
A similar argument can be made for the hardwood pulp, despite the fact that hydrogen peroxide treatment reduced lignin content in the DE pulp (in contrast to its performance on softwood DE pulp). However, hydrogen peroxided treatment was not nearly as effective as chlorine dioxide treatment. In every case, higher brightness would be expected whenever a D_2 stage precedes the P stage.

This hypothesis is also supported by monitoring the final brightnesses of pulps treated over a range of P-stage charges. **Figure 10** shows the final brightnesses of softwood DEDP and DEPD pulps over a range of hydrogen peroxide charges. As noted previously, the final DEPD brightnesses are lower than the DEDP sequence. Moreover, as the P-stage charge increases, the brightness development of the DEPD pulp is less than that of the DEDP pulp (as indicated by the flatter curve for DEPD). This indicates a limitation of the concentration 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 the presence of lignin that is less sensitive to reaction with hydrogen peroxide. This is supported by the structural evidence presented in this report.

KEYWORDS
Bibliographies, bleaching, chemical reactions, chemical treatment, chlorine dioxide, delignification, eucalyptus, hardwoods, hydrogen peroxide, kraft pulps, multistage process, oxides, processes, softwood pulps.

CONCLUSIONS

Various kraft pulps were bleached using ECF (elemental chlorine free) sequences containing a peroxide stage. Brightnesses were consistently higher when the second D stage (D_2) preceded the P stage(s). Analysis of the lignin extracted during the course of bleaching provides an explanation of this observation based on the known chemistry of chlorine dioxide and hydrogen peroxide with various lignin structures. In the case of DEDP sequences, the D_2 stage effectively removes lignin from the pulp and generates hydrogen peroxide-sensitive species. This improves conditions for the P stage and allows the pulp to achieve a higher brightness. Conversely, the hydrogen peroxide stage of the DEPD sequence is ineffective at lignin removal in softwood. The performance with hardwood pulps is better, with a 60–70% removal of lignin. Nevertheless, the P stage is less effective for lignin removal than the D_2 stage for both softwoods and hardwoods. Consequently, bleach sequences with a P stage preceding the D_2 stage will produce pulps with a lower final brightness. **TJ**



10. Effect of P-stage charge on final brightness of northern softwood pulps bleached with DEDP and DEPD sequences

Senior is a senior research chemist and Hamilton is a chemist at the Pioneer Technology Centre, 2101 Hadwen Road, Mississauga, ON, Canada L5K 2L3. Ragauskas is an associate professor, and Sealey and Froass are students at the Institute of Paper Science and Technology, 500 10th Street N.W., Atlanta, GA 30318.

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