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BLEACHING PROCESSES FOR MARKET GRADE TCF PULPS

J.L. Colodette, A.K. Ghosh, B. Dhasmana, U.P. Singh, J.L. Gomide and R.P Singh
North Carolina State University

ABSTRACT

Totally chlorine free bleaching processes aimed at producing fully bleached market grade softwood and hardwood pulps are evaluated. Processes including ozone and/or chelant and peroxide are described for a hardwood kraft-O pulp and processes including chelant, xylanase, ozone and peroxide are reported for softwood kraft-O pulps. Techniques aimed at minimizing ozone oxidation and alkaline peroxide depolimerization of carbohydrates during bleaching are explored. These include (1) methods to reduce the pulp lignin content arriving at the Z-stage such as extended delignification and peroxide delignification; (2) the use of enzymes to boost delignification; (3) the use of antioxidants such as DMSO in the ozonation; (4) the proper control of alkalinity and of peroxide stability in the P-stage following ozonation; and (5) the adequate location of metals removal stage(s) in the bleaching sequence.

Processes involving only chelant and peroxide are more attractive when the total charge of H_2O_2 is applied in a single stage, the use of conditions that favor controlled formation of hydroxyl radicals, *via* thermoinduction, being preferred. Such processes are recommended for bleaching hardwood kraft-O pulp to brightnesses in the range of 82-86 ISO. Bleaching processes involving ozone and peroxide are potentially the most attractive, the order of bleaching efficiency among the main combination of these two chemicals being QP(ZE)P > (ZE)QP > Q(ZE)P. The chemical costs and strength properties of a hardwood kraft-O pulp fully bleached by the sequence QP(ZE)P is comparable with those bleached by the conventional sequence DEopD.

Full bleaching of softwood kraft-O pulp is practicable by combination of chelant, ozone and peroxide in sequences such as QP(ZE)P and (ZE)QP but final viscosities are extremely low. The presence of an additional chelation stage such as in the sequence QP(ZE)QP considerably improve viscosity. Also, the use of DMSO enhance viscosity when applied to the Z-stage of the sequence QP(ZE)P. The conjunction of xylanase, ozone, chelant and peroxide in the sequence (X+Q)P(ZE)P applied to an extended delignified softwood kraft-O pulp result in full bleaching while maintaining the pulp strength properties at the same level of a similar pulp bleached conventionally.

Proper combination and optimization of bleaching stages is essential for successful bleaching. All P-stage(s) in the bleaching sequence must be anteceded by metals removal treatments. An alkaline extraction after ozonation increases the efficiency of the process especially when carried out without intermediate washing. A more efficient use of the peroxide in the bleaching process is achieved by dividing the total charge into two stages, with an intermediate ozonation. Conditions that favor hydroxyl radical delignification are encouraged in the first P-stage whereas conditions that minimize peroxide decomposition and reactions of its intermediates with partially oxidized carbohydrates be included in the last P-stage.

1. INTRODUCTION

The brightness target for market grade TCF pulps is increasingly raising as the demand for such pulps widens. In the past three years pulps semibleached (82-86 ISO) by processes based only on hydrogen peroxide and oxygen have been supplying the TCF market. However, after the implementation of the ozone bleaching technology at several mills in Scandinavia, the brightness requirements have gone up to the full brightness range (88^+ ISO).

Full bleaching by TCF processes has always been hampered by pulp quality concerns because such processes require the use of ozone. It has recently been reported that the cellulose depolimerization caused by ozone in TCF processes is not a problem for hardwood kraft and softwood sulphite pulps but it is a problem in the case of softwood kraft pulp (1). While such discovery is difficult to understand based on the process chemistry it may be rationalized on the basis of the higher charge of ozone required to bleach the softwood kraft pulp relative to the others.

The severe oxidation inflicted in the cellulose chains by the ozone leads to further depolimerization in a subsequent alkaline treatment, particularly oxidative ones (1). Thus, the successful production of market grade softwood kraft pulp *via* TCF processes demands the application of techniques that minimize such problems. The use of procedures that decrease the pulp lignin content arriving at the Z-stage such as extended delignification and peroxide delignification is a portentous alternative because it abbreviate the amount of ozone required for full pulp bleaching. Likewise, pulp pretreatment with enzymes such as xylanase may boost delignification during ozonation and abate ozone demand. On the other hand, the use of antioxidants such as DMSO in the ozonation may lower carbohydrate oxidation rates and increase the process selectivity. On the same line, the proper control of alkalinity in the P-stage following ozonation may cut down depolimerization and magnify process selectivity. Finally, the proper location of metals removal stage(s) in the bleaching sequence may minimize depolimerization by decreasing peroxide decomposition and free radical formation.

The evaluation of the aforementioned alternatives in connection with the bleaching of softwood and hardwood kraft-O pulps by TCF processes constituted the main objective of this investigation.

2. EXPERIMENTAL

Three well washed unbleached pulp samples were used (Table 1). An eucalyptus kraft-O from a South American mill (sample A), a pine kraft-O (sample B) and a pine kraft$_{ex}$-O (sample C) both from Southern U.S mills. Ozone was prepared at a concentration of 3-4% in the carrier gas by passing ultra high purity oxygen through an ozone generator at a voltage of 60-70 V. Except when stated otherwise, all other chemicals used were of reagent grade.

Ozonation was effected at ~40% consistency and ambient temperature on previously acidified pulps. The samples with or without additives were acidified to pH 2 with 4N H_2SO_4 at 3.5% consistency, kept at room temperature for 15 min and then dewatered to a consistency of about 37%. The pulp was then fluffed in a variable speed stainless steel fluffer and the consistency was determined. Immediately after, the ozonation was carried out on 25 g o.d. pulp samples in a 3-L glass flask which was adapted in a well-sealed rotary evaporator. Air was evacuated from the system prior to ozone injection and a stream of ozone of known concentration was injected into the rotating flask for an amount of time sufficient to give the desired consumption of ozone. Except when stated otherwise, at the end of the reaction the ozonated pulp samples were immediately extracted with NaOH without intermediate washing. The oxidative extractions reinforced with oxygen and hydrogen peroxide (Eop) were carried out on 150 g o.d. pulp samples in a Quantum - Mark III high shear mixer. Unless stated differently, all other bleaching stages were carried out according to well established procedures under the conditions shown in Table 2. The pH adjustments were effected using NaOH or H_2SO_4.

Brightness, kappa number, viscosity and strength properties of the pulps were determined according to Tappi standards. Pulp beating to various drainage degrees was carried out in a Jockro mill. The A.D. brightnesses were determined on air dried handsheets and the O.D. brightnesses determined on these same handsheets after oven drying at 105±3°C and 0% relative humidity for 60 min. Metals in the pulp were determined by neutron activation analysis. Ozone and peroxide residuals were determined iodometrically.

TABLE 1. Pulp samples characteristics.

PULP CHARACTERISTIC	SAMPLE A	SAMPLE B	SAMPLE C
Pulp Type	HWK-O	SWK-O	SWK_{EX}-O
Kappa Number	9.5	17.9	16.0
Viscosity, cP	27.9	25.8	29.8
Brightness, ISO	45.5	27.6	33.3
Iron, ppm	45.4	15.5	20.7
Copper, ppm	16.9	4.3	2.3
Manganese, ppm	321	61.7	18.3
Cobalt, ppm	0.02	0.02	0.04
Zinc, ppm	3.3	2.90	-
Magnesium, ppm	172	487	105
Calcium, ppm	-	658	587

TABLE 2. General Bleaching Conditions.

BLEACHING CONDITION	BLEACHING STAGE									
	Q	X	(X+Q)	E	Eop	P_1	P or P_2	Z	D_{100}	D
Consistency, %	3.5	10	10	10	10	10	10	40	10	10
Temperature, °C	70	70	70	70	70	var.	90	amb.	60	75
Reaction time, min	60	90	90	90	90	var.	var.	var.	60	210
Final pH	6.0	6.5	6.5	11.5	11.5	var.	var.	2.5	2.9	3.8
NaOH, % O.D.	-	-	-	2.0	2.0	var.	var.	-	-	-
Na_5DTPA 40%, % O.D.	0.5	-	-	-	-	-	-	-	-	-
Xylanase, % O.D.	-	0.044	0.044	-	-	-	-	-	-	-
Na_2SiO_3, % O.D.	-	-	-	-	-	3	3	-	-	-
Mg, % O.D.	-	-	-	-	0.05	-	-	-	-	-
O_2, % O.D.	-	-	-	-	0.4	-	-	-	-	-

3. RESULTS AND DISCUSSION

3.1. TCF BLEACHING OF HARDWOOD KRAFT PULP

There are a limited number of studies on TCF bleaching of hardwood kraft pulps, particularly of eucalyptus (2-7). By virtue of its lower lignin content and chemical nature, hardwood pulps usually bleach better than their softwood counterparts. The semibleaching of these pulps to brightness in the range of 82-86 ISO using only oxygen and hydrogen peroxide has been commercially demonstrated (7) but full bleaching will likely require ozone.

3.1.1. Bleaching With Hydrogen Peroxide Only

At least two kraft pulp (7,8) or kraft-O pulp (4,5,8,9) bleaching processes involving hydrogen peroxide as the only oxidizing agent are currently being used. Of these, the more well known is probably the "lignox" process, which was developed in 1989 by Eka Nobel (9,10). This process consists of treating the pulp with a chelating agent in the pH range 5-7 (Q) to reduce the negative effect of transition metals, followed by bleaching with hydrogen peroxide and/or chlorine dioxide in sequences such as QP, QPP, Q(Ep)D, etc. In 1991, a similar process for bleaching eucalyptus kraft and kraft-O pulps in which the pretreatment with chelant was replaced by an acid treatment (A) in a sequence of the type A(E+O+P)PP went into operation at Aracruz Celulose S/A (7). Similar studies with this sequence were carried out in the laboratory with eucalyptus (5,6) and other hardwood kraft pulps, including a comprehensive study on Eastern Canadian hardwood pulps (8).

A. Effect of peroxide distribution

The curves presented in Figure 1 show the effect of peroxide distribution on bleaching efficiency. For a fixed peroxide charge, the sequence QP resulted in higher brightnesses than the sequences QPP and QEopP, indicating that an even split of the peroxide charge between two stages was detrimental to the bleaching efficiency. A significant peroxide residual, in the range of 25-45% was maintained in all experiments used to generate the regression curves shown in Figure 1. The maintenance of high residuals was achieved through a rigorous control of alkalinity and reaction time during the bleaching.

Fundamentally, there exist two factors of vital importance in peroxide bleaching: 1) maintaining the peroxide stability through a rigorous control of transition metals in the system and 2) maintaining a high concentration of peroxide during the entire bleaching reaction. The first objective can be achieved through pulp pretreatment with acid or chelant and the use of proper peroxide stabilization systems. The maintenance of high peroxide concentrations during the reaction can be achieved by applying large doses of reagent and/or by bleaching at high consistency. The most practical option and the one most easily adapted to existing bleach lines is to use high peroxide charges in a single stage. This procedure favors delignification by hydroxyl radicals, especially when pH and temperature are properly controlled and peroxide stabilization is carried out suitably, so that the bleaching ends with a high residual of reagent. Such residuals can be used, for example, in the high density tower resulting in additional brightness gains.

Bleaching with high peroxide residuals has been applied with success in a two stage process for high yield pulps. This process, in which the total peroxide charge is applied in the second stage, permits almost total reuse of the high second stage residual (high consistency) in the first stage (medium consistency), because of the consistency difference between stages. However, medium consistency bleaching lines cannot efficiently take advantage of this process, and the installation of a high consistency bleaching stage may not be attractive for many mills given its high capital cost.

The use of a P or Eop stage after acid or chelation pretreatments is still a matter of controversy. The results presented in Figure 1 indicate that the sequence QEopP produces brightnesses similar or slightly inferior to those obtained with the sequence QPP for the same peroxide dosage. The additional oxidizing power of oxygen did not result in any benefit for the QEopP sequence. This unexpected result may be attributed to the fact that the pulp had previously been delignified with oxygen and therefore a limited number of reaction sites were available for attack by oxygen in the Eop stage. In the case of higher kappa pulps such as conventional kraft, benefits from the Eop stage will probably be more evident.

B. Effect of the temperature

Recently, a great number of studies (6-12) have demonstrated that significant quantities of lignin can be removed from kraft or kraft-O pulp during peroxide bleaching. This lignin removal has been attributed ultimately to the so-called delignification by hydroxyl radicals. The peroxide bleaching conditions which favor this delignification are substantially different from those conceived as optimum in peroxide bleaching of high yield pulps.

The results presented in Table 3 show the significant effect exercised by temperature during peroxide bleaching. Conventional peroxide bleaching technology foresees the use of temperature in the range of 70°C for greatest efficiency. However, if the system alkalinity is maintained sufficiently low as shown in Table 3 the use of high temperatures, which favor the formation of hydroxyl radicals *via* thermoinduction (13), results in greater delignification and bleaching efficiencies. Although not effective in bleaching reactions, hydroxyl radicals activate lignin toward subsequent pulp brightening by perhydroxyl anions during peroxidation (14). This mechanism explains the higher brightnesses obtained in the high temperature bleaching.

It is worth noting that a fraction of the lignin removed during peroxide bleaching actually occurs by alkaline leaching which is favored by the high temperatures and long retention times used in the process. The results in Table 3 show that up to 12% of the pulp lignin is actually removed by simple alkali extraction under the same conditions used in the P-stage.

3.1.2. Bleaching With Ozone and Hydrogen Peroxide

The results discussed in previous sections, especially those of Figure 1, clearly indicate that obtaining brightness values above 86 ISO using only hydrogen peroxide is no easy task. Although it is possible to reach brightnesses of 88^+ ISO in sequences such as QP, QPP or QEopP, the cost of reagents becomes prohibitive at these high brightness levels.

Excepting chlorine based compounds, there exists a limited number of products currently on the market capable of forming, with hydrogen peroxide, the highly sought after TCF sequence for bleaching kraft pulp to full brightness. These products can be summed up as enzymes, peracetic acid, permonosulphuric acid derivatives and ozone. Although there have been recent reports (15) that peracetic acid use in OPPaP* type sequences can produce pulps of 90 ISO brightness with acceptable properties, the majority of attention has been devoted to ozone because of its high standard reduction potential and its excellent delignification capacity.

TABLE 3. Effect of the reaction temperature on peroxide bleaching of a hardwood kraft-O pulp, SAMPLE A, pretreated with DTPA[1].

TEMPERATURE, °C	INITIAL pH	RESULTS AFTER P-STAGE[1]			RESULTS AFTER E-STAGE[2]		
		KAPPA DROP, %	VISC., cP	BRIGHT., ISO	KAPPA DROP, %	VISC., cP	BRIGHT., ISO
70	10.7	18.9	23.6	68.0	6.3	27.3	35.8
	11.2	20.0	22.6	68.6	7.4	27.8	36.3
	11.7	18.9	24.2	68.3	7.4	27.5	36.4
90	10.7	29.5	19.5	74.6	9.5	27.3	36.5
	11.2	28.4	19.8	74.3	10.5	27.2	36.3
	11.7	25.3	19.8	73.6	10.5	27.5	36.7
98	10.7	37.9	14.9	81.2	10.5	27.4	36.8
	11.2	35.8	15.2	80.9	11.6	27.2	36.7
	11.7	33.7	15.2	79.6	12.6	26.9	36.5

[1] Chelation treatment: 0.5% Na_5DTPA 40%, 70°C, 60 min, pH 6, consist. 3.5%.

[2] P-stage : 2.5% H_2O_2, 3% Na_2SiO_3, consist. 10%, 180-240 min

[3] E-stage: 3% Na_2SiO_3, consist. 10%, 180-240 min.

It is yet unclear the best way to combine ozone and peroxide in a bleaching sequence in order to reach high efficiency. Apparently, the most obvious position to apply ozone in a bleaching sequence is immediately after oxygen delignification, in order to activate pulp lignin and facilitate the subsequent bleaching (16). However, some reports (17,18) have suggested that removal of the relatively reactive and easily extractable lignin from the pulp after oxygen delignification by alkaline treatment, preferably in the presence of an oxidant, may raise the efficiency and selectivity of ozone bleaching. The use of hydrogen peroxide for this purpose leads to the sequence OPZP which was originally suggested by Kasseb and Gratzl (19) and more recently corroborated by other investigators (18,20).

Bleaching processes involving ozone and peroxide suggests the need for a metals removal step in order to achieve the full potential of these chemicals. The necessity and location of the metals removal step is a controversial matter. In the case of the OPZP sequence, the location of the metals removal stage is more obvious since it must precede the first peroxide stage, as in a OQPZP type sequence. However, in the case of the OZP sequence, there are doubts as to the necessity and best location of this step. Since ozone treatment is run under acidic conditions, it is doubtful whether a chelation treatment makes a significant contribution if applied before the ozonation, as in the sequence OQZP.

The results presented in Table 4 indicate that the inclusion of a chelation treatment significantly improves the bleaching of the kraft-O pulp by the sequences ZP and (ZE)P. In addition, the results also clearly demonstrate that this treatment is best located between the Z and P stages, in confirmation of Carre & Lindstrom's results (21).

Another controversial aspect of ozone/peroxide bleaching is whether or not a washing and/or extraction step is necessary after pulp ozonation. This topic has been treated in detail by Lindholm (22,23) in a series of articles in which the author suggests simple pulp neutralization in order to reduce the viscosity loss typical of alkaline stages following ozonation. The results presented in Table 4, for a kraft-O pulp, show that running an alkaline extraction after ozonation improves the performance of the bleaching sequences QPZP (tests 1 x 2), ZP (tests 3 x 4), QZP (tests 8 x 10) and ZQP (tests 6 x 7). On the other hand, the installation of a washing operation after the ozonation seems unnecessary, at least for the QZP sequence (test 8 x 9). This trend was also observed for a softwood kraft-O pulp (18).

TABLE 4. Effect of chelation, washing and alkaline extraction treatments on the performance of various bleaching sequences, SAMPLE A, optimized conditions.

TEST N°	SEQUENCE	O_3, % O.D.	H_2O_2, % O.D.	(ZE)-KAPPA	VISC., cP	A.D. BRIGHT., ISO	O.D. BRIGHT., ISO
1	QPZP[1]	0.55	1.00	1.7	12.5	88.7	86.3
2	QP(ZE)P[1]	0.55	1.00	0.8	12.8	89.8	88.0
3	ZP	0.80	1.00	2.4	10.9	85.3	82.4
4	(ZE)P	0.80	1.00	1.0	9.9	85.9	83.3
5	Q(ZE)P	0.80	1.00	1.1	8.7	88.5	86.8
6	(ZE)QP	0.80	1.00	1.0	10.4	89.4	87.0
7	(ZQ)P	0.80	1.00	1.7	10.6	87.9	86.8
8	QZP	0.88	1.00	1.9	8.1	87.8	86.8
9	Q(ZP)	0.88	1.00	-	10.9	88.2	86.3
10	Q(ZE)P	0.88	1.00	0.9	8.1	89.4	87.9
11	(ZE)QP	0.88	1.00	0.8	9.7	91.6	89.6

[1] H_2O_2 distributed evenly between P stages.

A. Optimization of the QP(ZE)P, Q(ZE)P and (ZE)QP sequences

On the basis of the results discussed in the preceding section (Table 4) the sequences QP(ZE)P, Q(ZE)P and (ZE)QP were selected for a study of optimization of reagent charges for bleaching kraft-O pulp to 90 ISO brightness. All bleaching variables were maintained constant as shown in Table 2 except for ozone and hydrogen peroxide charges. A factorial statistical design was applied and regression analyses were used to express brightness as a function of the doses of ozone and peroxide.

Two mathematical models were chosen for the QP(ZE)P sequence, one expressing brightness as a function of the reagent charge in the 1st and 2nd P stages and the Z stage and the other expressing brightness as a function of total peroxide and ozone charges (Fig. 2). An examination of variable coefficients indicates that the ozone dose is much more significant than the total peroxide dose while the dose of peroxide is more significant in the 1st P-stage than in the 2nd P-stage.

The curves in Figure 2 show that the order of bleaching efficiency of the sequences studied is: QP(ZE)P > (ZE)QP > Q(ZE)P. Although the Q(ZE)P sequence is more efficient than the (ZE)QP at low ozone doses, this result is of little meaning because achieving 90 ISO brightness by the Q(ZE)P sequence using low ozone doses is impractical due to the very high peroxide charge required.

Bleaching with ozone as well as peroxide is influenced by transition metals. It is therefore more logical to locate the chelation stage at the beginning of the bleaching sequence. The results shown in Figure 2 contradict this logic, at least for the higher ozone doses. The Q(ZE) and (ZE)Q kappa values shown in Table 4 for ozone doses of 0.8% (tests 5 x 6) and 0.88% (tests 10 x 11) indicate that chelation of the pulp before ozonation neither aided nor harmed the process significantly. The lower efficiency of the Q(ZE)P sequence may be explained by pulp contamination by metal ions between the Q and P stages, which may have harmed the P stage efficiency. This hypothesis may explain the superior results of the (ZE)QP sequence which is immune to such contamination.

The superiority of the QP(ZE)P sequence compared to the others is perfectly explained on the basis of the theory proposed by Gellerstedt (17) who recommends the removal of easily extracted and highly reactive lignin from the pulp before ozonation as a way to increase process efficiency and selectivity and to reduce ozone consumption. Additionally, the QP(ZE)P sequence possesses an additional bleaching stage compared to the others which increases the process efficiency. It is a recognized fact that longer bleaching sequences use reagents more effectively than short sequences.

In Figure 3 the chemical cost for bleaching the hardwood kraft pulp to 90 ISO by the 3 sequences above discussed at different reagent doses are compared with costs for the more conventional sequence DEopD. Cost of reagents were extracted from reference (8). It is indicated that the lowest cost TCF sequence is QP(ZE)P and that the cost of this sequence decreases with an increase in the applied ozone charge. In fact, the cost of this sequence can be quite similar to that of the reference DEopD sequence if a sufficient quantity of ozone is applied. The order of reagent costs to achieve 90 ISO brightness is DEopD < QP(ZE)P < (ZE)QP < Q(ZE)P.

B. Bleached Pulp Quality

As shown in Table 5, the viscosities of the pulps bleached by the TCF processes were inferior to that of the pulp bleached by the conventional sequence DEopD. However, their physical properties were comparable or in some cases superior to those of the pulp bleached by the conventional DEopD sequence. Special attention should be given to the pulp bleached by the QP(ZE)P sequence, which presented an 11% greater modulus of elasticity and an 18% greater inter-fiber bond strength than the pulp bleached by the conventional sequence. The pulps bleached by the TCF processes presented higher moduli of elasticity, tensile and burst indexes and lower tear indexes than those of the pulp bleached by the conventional DEopD sequence. The lower tear strength of these pulps may be explained by their lower viscosities. It is worth noting that the pulp bleached by the QP(ZE)P sequence (visc. 12.1 cP) presented a tear index very near that of the pulp bleached by the conventional sequence (visc. 20.3 cP). On the other hand, the pulp bleached by the Q(ZE)P sequence, which had a low viscosity (8.1 cP) due to its high ozone requirement, presented the lowest tear index. These results indicate that there exists a minimum viscosity value below which tear strength deterioration occurs. This minimum value seems to be in the range of 10 cP.

TABLE 5. Physical properties of TCF pulps (brightness 90±0.5 ISO), expressed at a sheet density of 594±0.5 kg/m^3, SAMPLE A.

RESULTS	KRAFT-O PULP	BLEACHING SEQUENCE				
		DEopD	QP(ZE)P	Q(ZE)P	(ZE)QP	QP
O_3, % O.D.	-	-	0.65	0.93	0.81	-
H_2O_2, % O.D.	-	0.5	1.00	1.00	1.00	12.0
ClO_2, % O.D.	-	2.01	-	-	-	-
A.D. Brightness, ISO	45.5	89.9	90.3	89.9	89.5	90.0
O.D. Brightness, ISO	-	87.9	88.1	88.0	87.7	88.0
Viscosity, cP	27.9	20.3	12.1	8.1	10.1	13.2
Tensile Index, N.m/g	110	90.1	95.0	97.4	96.4	98.8
Tear Index, mN.m^2/g	10.4	10.6	10.0	8.5	9.5	9.3
Burst Index, kPa.m^2/g	7.2	5.1	5.9	5.6	6.0	6.1
Stretch, %	2.7	3.0	3.1	2.9	3.1	3.1
Inter-fiber bond strength, J/m^2 (*)	10.5	12.3	14.6	12.8	13.6	13.5
Tensile Energy Absorption, J/m^2	120	118	123	115	121	124
Stress at Lim. of Proport., MPa	25.0	21.1	21.4	22.1	20.2	22.2
Strain at Lim. of Proport., %	0.428	0.519	0.503	0.496	0.503	0.507
Specific Modulus of Elastic. , MN/m.kg	8.9	7.0	7.2	7.7	7.1	7.7

(*) Measured on unbeaten pulp samples (density = 248-312 kg/m^3).

3.2. TCF BLEACHING OF SOFTWOOD KRAFT PULP

The results discussed in the previous section demonstrate that full bleaching of hardwood kraft-O pulp is successfully accomplished using combinations of chelant, ozone an hydrogen peroxide in sequences such as QP(ZE)P and (ZE)QP. Furthermore, the quality of the TCF bleached pulp is comparable to those of the same pulp bleached conventionally. On the other hand, the results shown in Table 6 indicate that TCF bleaching of a softwood kraft pulp is not so easy. The brightness target of 88$^+$ is attained by the sequence QP(ZE)P but the final viscosity is quite low. The difficulty in bleaching softwood pulps compared to hardwood ones stems from their higher lignin content, the chemical nature of their lignin and their homogeneously lignin distribution in the fiber wall. These altogether lead to higher bleaching chemical requirements and, consequently, to lower bleached pulp viscosities. Conventionally cooked softwood kraft pulps will usually have a kappa number about two-fold higher than their hardwood counterparts after oxygen delignification but a similar viscosity (Table 1). This situation in itself put softwood pulps in great disadvantage for TCF bleaching in comparison to hardwoods.

TABLE 6. Bleaching of a conventional softwood kraft-O pulp by selected sequences, SAMPLE B.

SEQUENCE	O_3, % O.D.	H_2O_2, % O.D.	(ZE)-KAPPA	VISC., cP	A.D. BRIGHT., ISO	O.D. BRIGHT., ISO
QP(ZE)P[1]	0.4	5.0		8.3	85.6	-
QP(ZE)P[1]	0.6	5.0		7.6	89.0	-
(ZE)P	1.2	2.5	2.9	7.1	77.3	76.0
(ZE)QP	1.2	2.5	2.9	7.4	85.2	82.0

[1] H_2O_2 distributed evenly between P stages.

The more obvious alternative to make TCF bleaching of softwood kraft pulp feasible is by extending the delignification during cooking so as to achieve lower kappa values after oxygen delignification. Other alternatives may include the use of enzymes to boost bleaching efficiency, the use of antioxidants in the Z-stage and adequate optimization of the last P-stage. These topics are addressed in the next sections.

3.2.1. The Effect of DMSO in the Z-stage

A certain amount of metals always slips trough metals removal treatments and inevitably will cause ozone and peroxide decomposition during bleaching. The ozone and peroxide decomposition intermediates, e.g. hydroxyl radical, can be harmful to bleaching selectivity although in many cases useful to bleaching itself. The use of additives to control the metals and/or these decomposition intermediates is sometimes desirable. Limited results reported in one of our previous work (24) indicated that DMSO is a potentially useful additive to enhance ozone bleaching selectivity. The more elaborate study shown in Table 7 confirm this finding showing that DMSO can indeed result in bleached pulp of higher viscosity if applied in the Z-stage (Z_D) of the sequence. The benefits of DMSO addition to the Z-stage were more significant for the sequence QP(ZE) where it resulted in a c.a. 40% viscosity increase for both ozone charges of 0.8 and 1.0%. For the sequence (ZE), the improvement in viscosity was c.a. 13% only. The reason why DMSO performed better for the QP-treated pulp than for the untreated one is currently unknown. A tentative explanation can be given by assuming that the QP-treated pulp gives rise to less free radicals during ozonation than the untreated pulp because of its lower concentration of transition metals (removed by chelation) and lower content of highly reactive lignin (removed by peroxide oxidation). Thus, it can be speculated that in a low free radical concentration system the DMSO may perform better as a scavenger than in a high free radical concentration system, whereby it may be destroyed by such radicals.

It should be pointed out that DMSO retard somewhat the rate of delignification during ozonation as indicated by the slightly higher kappa number and slightly lower brightness values of the DMSO treated samples compared to the untreated ones. This can be explained by the decreased rate of delignification by hydroxyl radicals when ozonation is carried out in the presence of DMSO. Hydroxyl radicals react 5-6 times faster with lignin-like structures than with carbohydrate-like structures (25) but, the ratio lignin:carbohydrate in pulp samples usually subjected to ozonation is in the range of 1-3:99-97%. Thus, hydroxyl radical tend to be a very unselective oxidizing agent during ozonation, even though it preferably reacts with lignin-like structures.

It is worth noting, however, that the substantial gain in selectivity due to DMSO addition turns irrelevant the small loss of delignification efficiency.

TABLE 7. Effect of DMSO[1] addition in the Z-stage on the performance of various bleaching sequences, SAMPLE B.

SEQUENCE	O_3, % O.D.	H_2O_2, % O.D.	(ZE)-KAPPA	VISC., cP	A.D. BRIGHT., ISO
(ZE)	0.6	-	9.6	15.9	39.5
(Z_DE)	0.6	-	10.0	18.2	39.2
QP(ZE)	0.8	2.5	1.4	8.7	76.0
QP(Z_DE)	0.8	2.5	1.7	14.5	73.5
QP(ZE)	1.0	2.5	1.0	7.7	79.8
QP(Z_DE)	1.0	2.5	1.3	13.1	75.8
QP(Z_DE)P[2]	1.0	4.5	1.3	9.2	91.6

[1] 4% DMSO o.d. pulp wt. at 40% consistency

[2] H_2O_2 distribution : 2.5% in 1st P and 2.0% in 2nd P.

3.2.2. Optimization of Last P-stage

By virtue of the low lignin content in the pulp after ozonation, conditions that favor peroxide brightening rather than delignification are advisable in the P-stage subsequent to ozonation. Due to its high carbonyl contents, pulps treated with ozone are highly sensitive to alkali degradation, thus requiring mild peroxide bleaching conditions.

The results presented in Table 8 show the effects of pH and of the alkali source on the bleaching performance of a P-stage applied to pulps pretreated by the sequence $QP_{2.5}(Z_{0.6}E)$. It is apparent that higher brightnesses are achieved at pH values lower than usual for peroxide bleaching but very low pH values which imply excessively long retention times are harmful to viscosity. Sodium silicate was proven the best alkali source with regard to brightness, a result attributable to silicate's well known functions as a buffer and peroxide stabilizer. However, sodium hydroxide alone is almost as good as silicate provided that the reaction is maintained at a very low rate by lowering the pH. The lowest brightness values were obtained with sodium carbonate, a somewhat unexpected result giving carbonate's apparent suitability as a base for peroxide bleaching at low alkalinities. The rather quick peroxide consumption in the presence of carbonate has not yet been rationalized.

The reason why peroxide consumption rates are very high on ozonated pulps is not clear. It is probably true that the residual lignin after ozonation is highly reactive but the amount of such lignin is very low to result in total consumption of large amounts of peroxide. On the other hand, the large amount of carbonyl structures generated in the carbohydrates during ozonation may somehow be responsible for the large peroxide consumption. Furthermore, it may be speculated that peroxide decomposition is substantial in the last P-stage because transition metals may be released from the fiber matrix during ozonation and become more effective catalysts in the subsequent P-stage. The latter may be the best explanation for the high peroxide consumption after the (ZE)-stage given the fact that a chelation treatment between the (ZE)- and P-stage(s) resulted in improved last P-stage performance (Table 9).

When a chelation is inserted between the (ZE)- and P-stages, higher alkalinities are necessary to consume the peroxide in a reasonable reaction time of 2 hs for example and improve brightness and viscosity (Table 10). Thus, the use of low alkalinity is recommended only if no chelation is applied prior to the last P-stage. It is worth noting that the same type of tendencies observed and explanations offered for the behavior of the last P-stage of the sequences QP(ZE)P and QP(ZE)QP are applicable for the P-stage of the sequences Q(ZE)P and (ZE)QP.

Rather low viscosities were obtained in the experiments carried out at a very low pH during an extended retention time (Table 8). This extensive carbohydrate degradation may be attributed to hydroxyl radical induced cleavage of glucosidic bonds which are favored in the lower pH range. Thus, effective pH control is very important in the P-stage following ozonation. Low alkalinities favor bleaching by preventing peroxide decomposition but also favor pulp degradation due to extended exposure of the fibers to hydroxyl radicals. On the other hand, high alkalinities will favor decomposition, especially in bleaching sequences not containing a chelation treatment between (ZE)- and P-stages.

3.2.3. The Effect of Extended Delignification

The results presented in Table 11 denote that the extended delignified kraft-O pulp bleach better than the conventional one regardless of the bleaching sequence. In general, this pulp required less ozone and peroxide than the softwood kraft-O to reach full brightness. As a result, higher final viscosities were attained. It is worth noting that fully bleached pulp of acceptable viscosity was also reached with the softwood kraft-O pulp by the sequence QP(ZE)QP. The second chelation stage proved instrumental to increase brightening efficiency and minimize viscosity loss in the last P-stage.

Extended delignification proved to be a consequential alternative for TCF bleaching because it results in decreased chemical costs and increased process flexibility as far as the final brightness and viscosity targets achievable.

3.2.4. Using Xylanase as a Booster in the Bleaching Process

The location of the xylanase treatment in a TCF bleaching sequence is still a matter of discussion. Despite the fact that the reaction conditions required for the xylanase treatment are somewhat similar to those used for pulp chelation the results shown in Table 12 indicate that the xylanase treatment perform better when applied separately from chelation. Nevertheless, for the sequence QP(ZE)P such a treatment seems better fit in combination with chelation in a single stage, (X+Q), since it produces final brightness only slightly lower than the two stage process, XQ or QX, but it is of much more practical application. On the other hand, for the sequences (ZE)QP and Q(ZE)P, the xylanase treatment is significantly more efficient when effected separated from chelation. Furthermore, the most attractive mode of xylanase and chelant application proved to be in the sequence X(ZE)QP.

TABLE 8. Effect of the alkalinity and alkali source on peroxide bleaching of a pulp previously treated by the sequence $QP_{2.5}(Z_{0.6}E)^1$, SAMPLE B.

SECOND P-STAGE[2]								
Na_2SiO_3, %	Na_2CO_3, %	NaOH, %	pH In	pH Out	Reaction Time, min	H_2O_2 Consumed, %	Brightness, ISO	Visc., cP
0.75	-	-	9.34	4.58	255	86.3	87.5	4.6
3.00	-	-	9.84	7.31	265	78.7	89.0	8.3
5.00	-	0.53	10.44	10.21	88	76.0	86.1	10.6
-	0.125	-	9.31	5.04	210	85.3	86.0	5.8
-	0.55	-	10.03	9.94	10	94.4	81.2	10.8
-	7.75	-	10.47	10.48	10	100	80.8	13.2
-	-	0.04	9.30	3.69	345	80.2	87.8	3.7
-	-	0.10	9.93	6.59	199	90.2	85.5	7.9
-	-	0.23	10.49	9.89	11	90.7	80.9	13.8

[1] $QP_{2.5}(Z_{0.6}E)$ sample: kappa 1.9, viscosity 15.2 cP, brightness 68.7 ISO.
[2] Second P-stage: 2.5% H_2O_2, 90 °C, 10% consistency.

TABLE 9. Effect of double chelation on TCF bleaching performance, SAMPLE B.

SEQUENCE	O_3, % O.D.	H_2O_2, % O.D.	VISC., cP	A.D. BRIGHT., ISO
QP(ZE)P[1]	0.4	5.0	8.3	85.6
QP(ZE)QP[1]	0.4	5.0	9.9	87.6
QP(ZE)P[1]	0.6	5.0	7.6	89.0
QP(ZE)QP[1]	0.6	5.0	9.6	90.5

[1] H_2O_2 distributed evenly between P stages.

TABLE 10. Effect of the alkalinity on peroxide bleaching of a pulp previously treated by the sequence $(Z_{0.8}E)Q^1$, SAMPLE C.

P-STAGE[2]							
Na_2SiO_3, %	NaOH, %	pH In	pH Out	Reaction Time, min	H_2O_2 Consumed, %	Brightness, ISO	Viscosity, cP
3	0.8	10.49	10.14	120	31.0	79.2	12.2
3	1.2	11.07	10.69	120	48.0	82.4	11.6
3	1.8	11.53	11.18	120	82.0	84.5	10.6

[1] $(Z_{0.8}E)Q$ sample: kappa 4.7, viscosity 13.6 cP, brightness 53.8 ISO
[2] P-stage: 3.0% H_2O_2, 90 °C, 10% consistency.

TABLE 11. Effect of the extended delignification on TCF bleaching performance.

SEQUENCE TYPE	O_3, % O.D.	H_2O_2, % O.D.	VISC., cP	A.D. BRIGHT., ISO
SOFTWOOD KRAFT-O PULP (SAMPLE B):				
$(Z_{1.2}E)QP_{4.0}$	1.2	4.0	6.4	86.5
$QP_{2.5}(Z_{1.0}E)P_{1.5}$	1.0	4.0	6.8	90.3
$QP_{2.5}(Z_{0.6}E)QP_{2.5}$	0.6	5.0	9.6	90.5
EXTENDED DELIGNIFIED SOFTWOOD KRAFT-O PULP (SAMPLE C):				
$(Z_{1.0}E)QP_{3.0}$	1.0	3.0	6.8	87.8
$QP_{2.5}(Z_{0.6}E)P_{0.5}$.	0.6	3.0	9.8	88.6
$QP_{2.5}(Z_{0.6}E)QP_{0.5}$	0.6	3.0	10.4	89.8

The benefits of using xylanase to increase brightness ceiling and decrease active chlorine consumption in conventional bleaching processes is well documented (26,27). However, there is only fragmentary evidence indicating the advantage of xylanase application in the bleaching with oxygen derived chemicals (28,29). Purportedly such a treatment may save ozone and/or peroxide, increase brightness ceiling and more importantly improve viscosity of TCF bleached pulps.

TABLE 12. Effect of the X-stage location on the performance of the sequences QP(ZE)P, Q(ZE)P and (ZE)QP, SAMPLE C.

X-STAGE LOCATION	O_3, % O.D.	H_2O_2, % O.D.	(ZE)-KAPPA	VISC., cP	A.D. BRIGHT., ISO
SEQUENCE QP(ZE)P:					
QP(ZE)P[1]	0.6	3.0	2.1	8.4	88.1
(X+Q)P(ZE)P[1]	0.6	3.0	1.5	8.8	89.4
XQP(ZE)P[1]	0.6	3.0	1.6	8.9	90.1
QXP(ZE)P[1]	0.6	3.0	1.5	8.8	89.9
SEQUENCES Q(ZE)P and (ZE)QP:					
Q(ZE)P	0.8	3.0	4.6	9.8	77.9
(X+Q)(ZE)P	0.8	3.0	5.0	9.5	79.3
QX(ZE)P	0.8	3.0	5.1	10.3	83.9
XQ(ZE)P	0.8	3.0	4.7	10.1	84.2
(ZE)QP	0.8	3.0	4.7	10.6	84.4
X(ZE)QP	0.8	3.0	4.0	9.8	87.1

[1] H_2O_2 distributed evenly between P stages.

The curves shown in Figure 4 reveal the ozone and peroxide requirements to bleach a Kraft$_{ex}$-O pulp to 88 ISO brightness by sequences with and without a xylanase treatment. The results estimated through the regression equations indicate that the introduction of the xylanase treatment saves 1-30% H_2O_2 or 1-18% O_3 depending upon the bleaching sequence and ozone/peroxide charges used. The effect of the xylanase treatment was proven more evident at the lower charges of peroxide and higher charges of ozone.

The results of selected experiments presented in Table 13 indicate that xylanase treated pulps possess higher viscosities than the untreated ones at a similar final brightness. This result stems from the lower requirements either of peroxide or ozone of these pulps compared to the untreated ones to reach a similar brightness target.

TABLE 12. Optimized results showing the effect of xylanase[1] on O_3 and H_2O_2 requirements, SAMPLE C.

RESULTS	BLEACHING SEQUENCE					
	(ZE)QP	X(ZE)QP		QP(ZE)P*	(X+Q)(ZE)QP	
		A*	B		A*	B
O_3, %	1.00	1.00	0.82	0.60	0.6	0.50
H_2O_2, %	3.00	2.00	3.00	3.00	2.5	3.0
(ZE)-Kappa	3.2	3.1	-	2.1	1.5	-
Brightness, ISO	88.0	88.2	87.8	88.1	88.2	87.7
Viscosity, cP	6.5	7.3	8.1	8.4	9.4	10.0

[1] Xylanase (X) treatment : 0.044% xylanase, 70°C, 90 min, pH 6.5, 10% consistency.

* Samples used for physical strength determinations.

3.2.5. Pulp Quality

Fully bleached pulp samples (88$^+$ ISO) were produced by selected sequences using optimum conditions according to the best techniques described in the previous sections. The physical strength of these samples, which are marked with asterisks and characterized in Table 12, were determined and compared with those of a sample bleached by the sequence DEopD at a similar brightness. The tear-tensile relationships shown in Figure 5 suggest that the several pulps behave somewhat similarly during refining. Although the tensile strength developed in the same way for all sequences, the tear indexes of the pulps bleached by the sequences QP(ZE)P and X(ZE)QP were lower than that of the pulp bleached conventionally. The lower tear strength reflects more celulose degradation in these TCF bleached pulps as denoted by their lower viscosity. However, there seems to exist a limiting viscosity value above which tear strength is not impaired. The tear-tensile relationship of the pulp bleached by the sequence (X+Q)P(ZE)P (9.4 cP) is equal or slightly superior to that of the conventional sequence (14.2 cP) despite its lower viscosity. Obviously, this limiting value may depend on the type of fiber and pulping and bleaching processes used.

The curves shown in Figure 5 demonstrate that is feasible to bleach softwood kraft pulp by TCF processes while maintaining pulp strength. This will require extended delignification and likely the application of an enzymatic treatment in the bleaching process such as in the sequence (X+Q)P(ZE)P.

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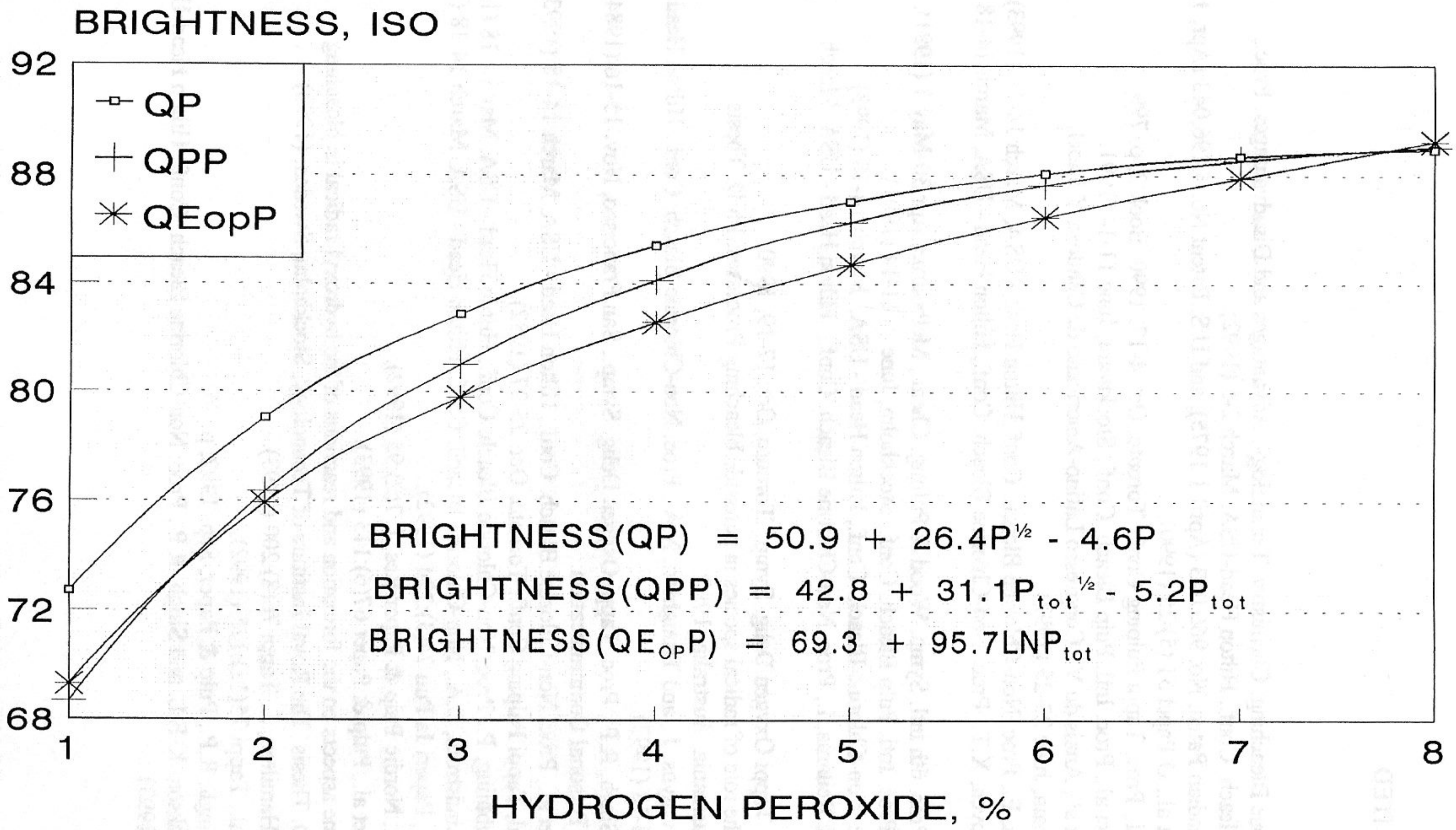

Figure 1. Effect of the peroxide charge on the bleaching of eucalyptus kraft-O pulp by the sequences QP,QEopP and QPP, under optimized conditions of alkali, temperature, reaction time and peroxide consumption. (Even split of peroxide between stages in the sequences QEopP and QPP).

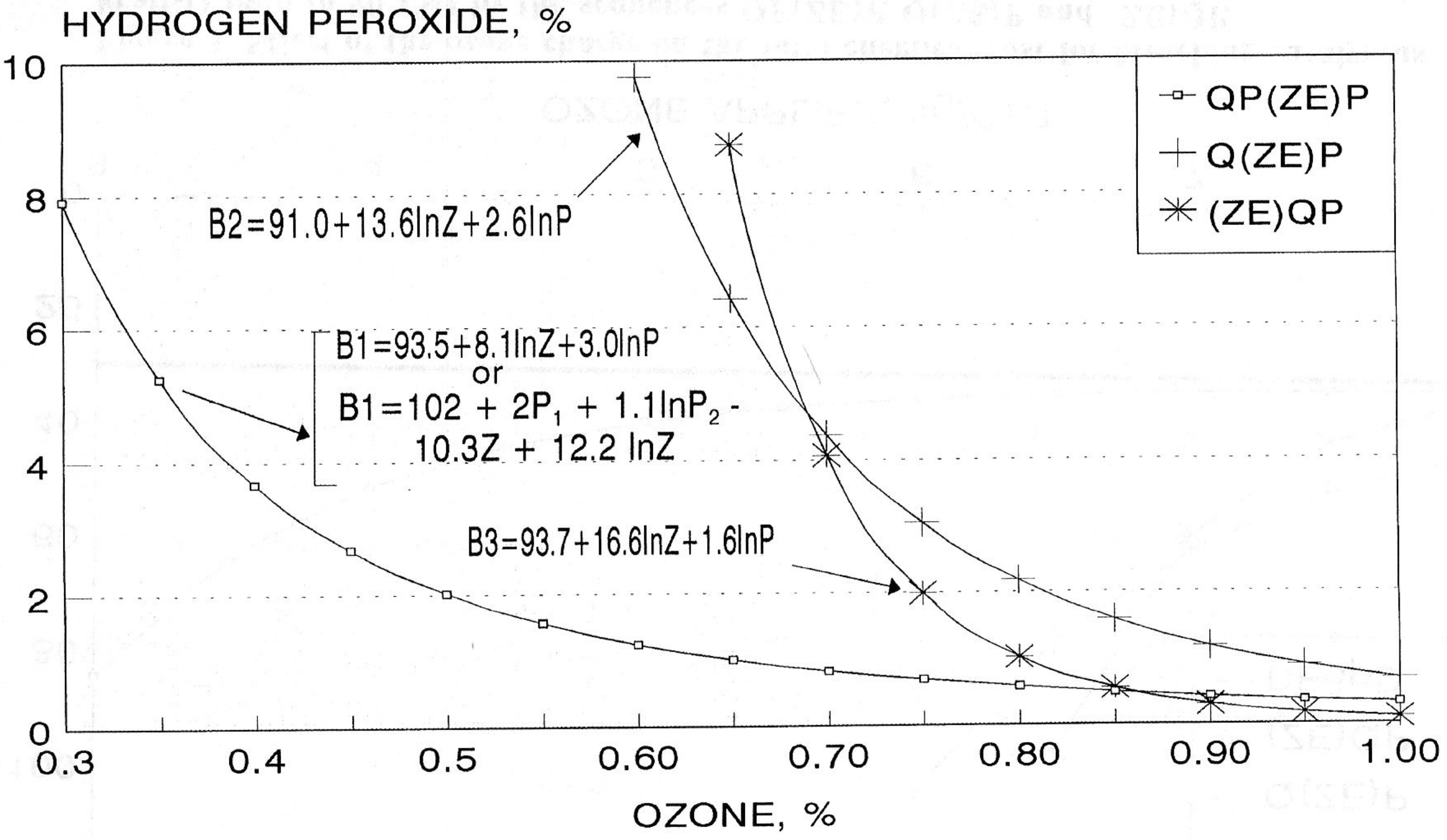

Figure 2. Curves of 90 ISO brightness as a function of the total charges of ozone and hydrogen peroxide. (Eucalyptus kraft-O pulp).

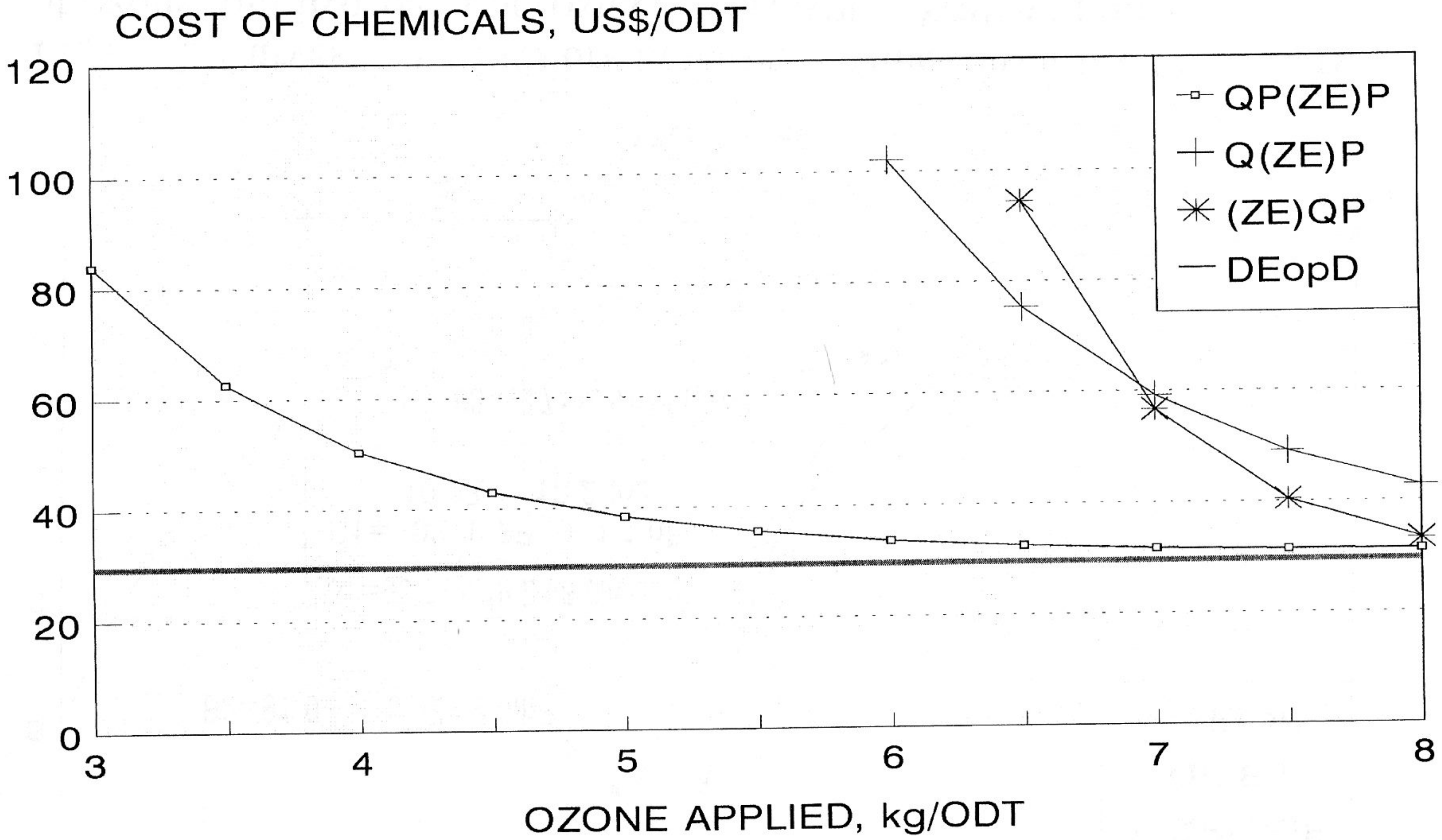

Figure 3. Effect of the ozone charge on the total chemical cost for bleaching eucalyptus kraft-O pulp to 90 ISO by the sequences QP(ZE)P, Q(ZE)P and (ZE)QP.

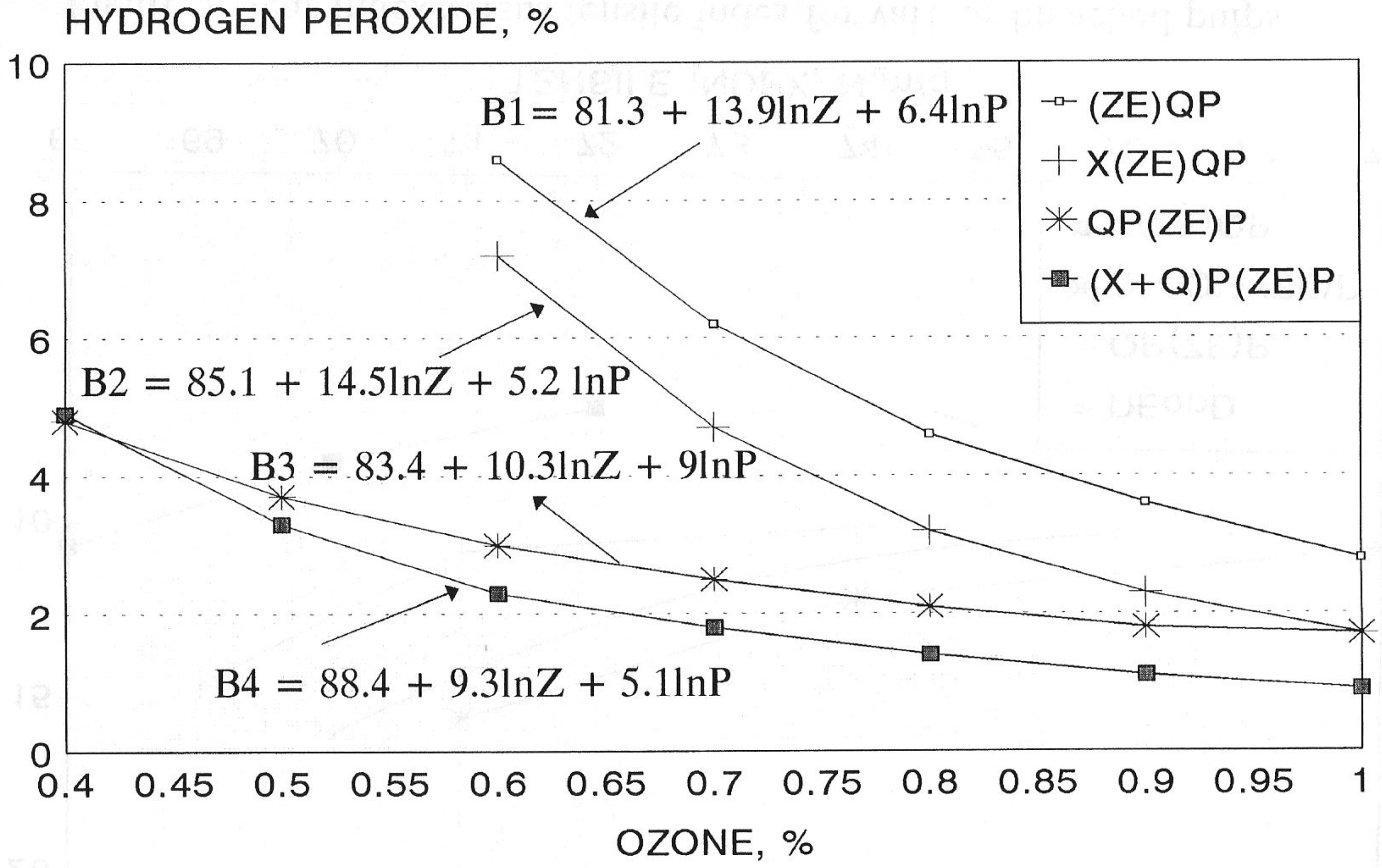

Figure 4. Curves of brightness 88 ISO as a function of the total charges of ozone and peroxide.(Softwood k_{EX}-O pulp).

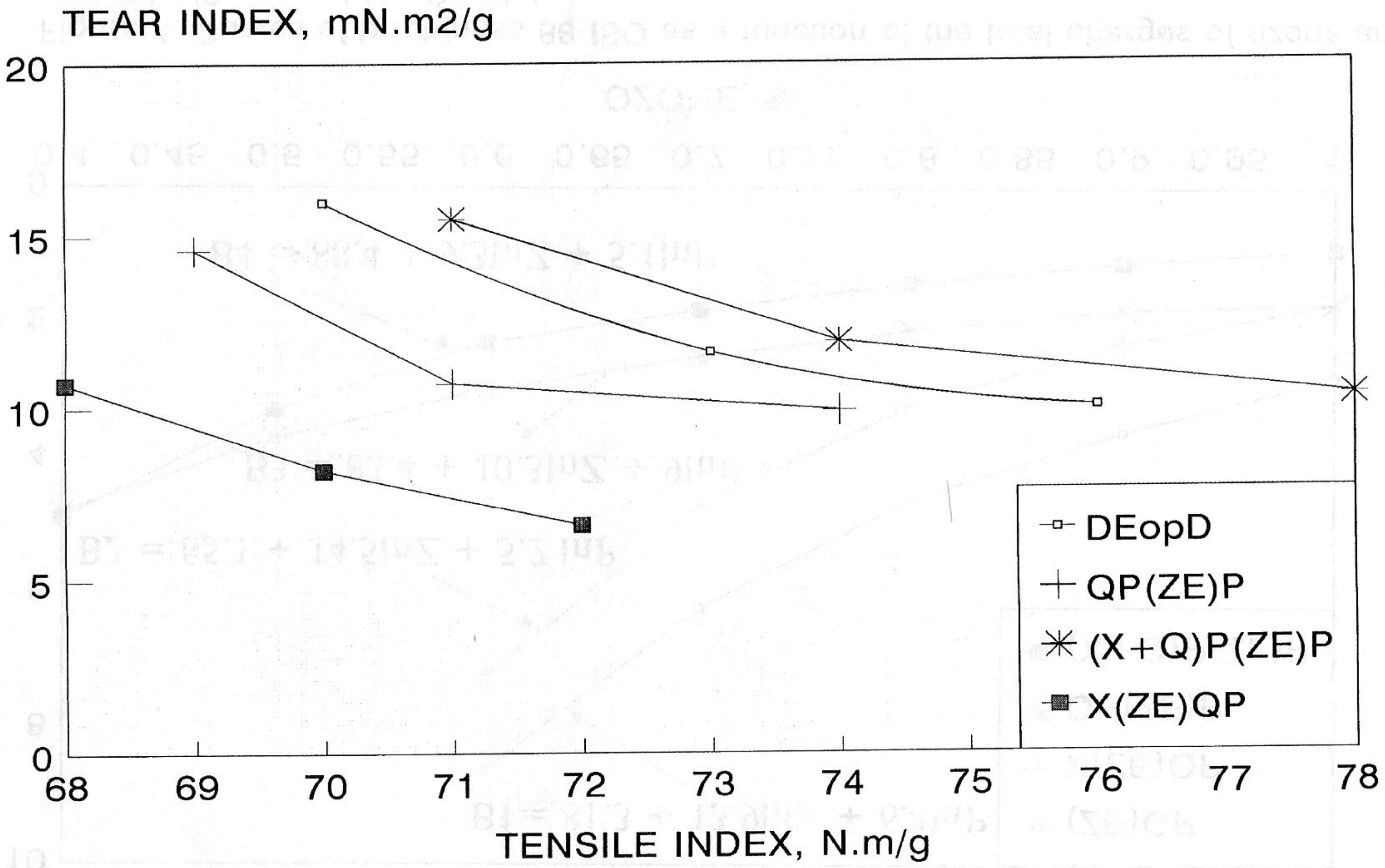

Figure 5. Tear index versus tensile index for various bleached pulps (softwood K_{EX}-O pulp).