The effect of phosphonates on kraft pulping and brown stock washing of eucalypt pulps

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SUMMARY

This work studied the effect of phosphonates on kraft cooking of mixed eucalypt chips (predominantly *E. grandis*) and brown stock washing of the resultant pulp. Results show that DTPMPA (diethylene triamine penta methylene phosphonic acid) is effective in reducing metal ions when applied in brown stock washing, producing improved pulp physical properties compared to the control. SPAP (sodium salt solution of polyaminophosphonic acids) increased pulp physical properties when applied only in cooking, but it showed best metals removal when dosed in brown stock washing. Another phosphonate, known as HEDP (1-hydroxy ethylidene diamine 1, 1-diphosphonic acid), EDTA (ethylene diamine tetra acetic acid), and strong acid washing were compared with DTPMPA and SPAP. DTPMPA and SPAP addition did not produce significant differences in Mg, Cu and Fe content in pulps, but Mn was reduced to very low levels. HEDP did not produce any difference in metal ions content compared with an untreated pulp.

Keywords
Kraft pulping, kraft pulps, TCF bleaching, chelating agents, phosphonates, brown stock washing

Kraft is the predominant chemical pulping process; however, there is continued pressure to improve the environmental performance by introducing improved chlorine free bleaching processes (ECF and TCF). As a consequence the use of chelating agents will increase in the future. Using O_2 delignification, it is possible to reduce Kappa number by about 50% without an equivalent decline in pulp quality (*1*). This would reduce the quantities of organic and inorganic products produced in pulp bleaching, and discharged in the effluents.

TCF pulps have generally lower strength properties than ECF as a result of cellulose depolymerisation. This is mostly caused by the action of hydroxyl radicals (HO•), which are extremely and indiscriminately reactive. The hydroxyl radicals are generated by peroxide decomposition, which is catalysed by metal ions present in the pulp (*2*).

As hydrogen peroxide is an intermediate in the stepwise reduction of O_2 in oxygen delignification, the hydroxyl radicals can also be produced in this stage (*3*). This reaction results in carbohydrate degradation and is catalysed by metal ions, particularly Mn^{+2}, Fe^{+3}, and Cu^{+2}. These metals also affect pulp physical and optical properties, fibre surface charge and swelling capacity (*4*).

Controlling organic peroxides formation and reaction will thus promote better pulp brightness and physical properties. Since wood contains Mn^{+2}, Fe^{+3} and Cu^{+2}, metals management in an early stage of pulp production would be advantageous, especially controlling organic peroxides formation before or during the O stage.

Mn levels less than 1 ppm are ideal, and to achieve these very low metal values, it would be necessary to use more than one chelating stage (Q). Pulp pretreatment in such a separate Q stage is usually performed to eliminate heavy metals and prevent peroxide decomposition (*5,6*). However, chelating agents may be added at several points in a TCF sequence.

The most commonly used chelating agents in the pulp and paper industry are EDTA (ethylene diamine tetra acetic acid) and DTPA (diethylene triamine pentaacetic acid). Other sequestrants more recently introduced are HEDTA (hydroxyethylene diamine tetra acetic acid), and phosphonates such as DTPMPA (diethylene triamine penta (methylene phosphonic acid)) and HEDP (1-hydroxy ethylidene diamine (1, 1-diphosphonic acid)). SPAP (sodium salt solution of polyaminophosphonic acids), is rarely used for this purpose.

An important aspect to consider in chelant selection is pulp pH. While EDTA requires acidic conditions, DTPA, DTPMPA and HEDP (*7*) function in strong alkaline medium, making it possible to use them in kraft pulping (*8*). In spite of this, there are few reports of addition of such chelating agents to the digester (*9,10*).

A separate acidic Q stage involves sulfuric acid addition and supplementary equipment making it an expensive option.

Hexenuronic acid groups, which readily consume electrophilic bleaching chemicals such as chlorine dioxide, ozone and peracids (*11*), are usually eliminated using an acid treatment. They are however unreactive in alkaline oxygen and peroxide bleaching stages. Thus in this case, an intermediate acid stage treatment can reduce bleaching costs. Hexenuronic acid groups are responsible for the low brightness stability of TCF pulps (*12*), hence colour reversal could be an issue if an acid stage is not used.

The different chelants do not perform in the same way with eucalypt kraft pulping and bleaching. Depending on mill conditions, wood characteristics and pulp metal ion concentrations, different metal management strategies may be necessary.

This study evaluates the application of various chelants in the kraft process prior to the oxygen delignification stage. Phosphonates, DTPMPA and SPAP, were added in the digester white liquor, and in brown stock washing, and their performance in brown stock washing was compared with the use of conventional acid HEDP and EDTA stages.

EXPERIMENTAL

Materials

Eucalypt air-dried chips (predominately *E. grandis*) were collected from the Celulosa Argentina, Capitán Bermúdez mill. Solutia Inc supplied the phosphorates.

Cooking

Chips were classified with a square mesh screen; retaining the fraction between

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Table 1
Kraft pulping conditions.

Wood moisture content, %	30.4
Active alkali, % on o.d. wood	22
Effective alkali, % on o.d. wood	19.0
Sulfidity, % on o.d. wood	27
Liquor/wood ratio	4/1
Maximum temperature, °C	168
Time to maximum temperature, min	90
H Factor	600

25 mm and 5 mm. Knots and bark were removed by hand.

Air-dried chips equivalent to 900 g (o.d.) were kraft pulped in an M/K System 10-L digester to a Kappa number of 16 to 17. Each batch was replicated to determine experimental errors. Cooking conditions are given in Table 1.

DTPMPA and SPAP were added in cooking and brown stock washing following a 2^2 factorial experimental design (Table 2). Chelant charge to each stage was 0.1% (active acid base) on o.d. chips, or pulp, respectively.

Washing

Brown stock washing was standardised as follows to obtain similar COD values before the oxygen stage:

1. Black liquor was drained immediately after finishing the pulping stage. A first washing was applied directly in the digester, recirculating 3.0 L of water for 10 minutes at 70ºC.
2. The chips were transferred to a 40 L plastic pulper and disintegrated at 3.0% stock concentration for 20 minutes at 58ºC. The chelant was then added and the pulp centrifuged.
3. A washing-screening stage was performed in a modified stainless steel Somerville screen using 26 L of recirculation water, then the pulp was centrifuged to 30% solids.

Table 2
Experimental design for kraft pulping and brown stock washing. (2^2 factorial design).

Treatment	Q in cooking	Q in brown stock washing
1	Without Q	Without Q
2	Without Q	With Q
3	With Q	Without Q
4	With Q	With Q

Chelant addition during washing

For this study a single pulp (50.6% unscreened pulp yield) was divided into equal fractions to ensure equivalent starting conditions. The washing stage was standardised as detailed above.

Trials involved EDTA, sulfuric acid, and DTPMPA, HEDP and SPAP addition in brown stock washing. Chelant agent charge in the washing stage was always 0.1% (active acid base) on o.d. pulp. Both acid treatments were applied in the third washing stage. DTPMPA, SPAP, and HEDP, were added in the second of three brown stock washing stages.

Testing

TAPPI standards were used for most tests (Kappa number, viscosity, and physical properties), except for Brightness (ISO 3688:1977) and opacity (ISO 2471:1977).

Pulp metal ion (Fe, Cu, Mg, and Mn) content was analysed by atomic absorption spectroscopy (TAPPI T266 om-94).

COD was tested on spent liquors, and on brown stock washing water, to determine the organic charge to the following step (CPPA st. H.3P).

RESULTS AND DISCUSSION

A sample of the eucalypt chips was calcined, without prior milling to avoid contamination, and the metal ion content determined (Table 3) as for the pulp samples.

Table 3
Metal ion content of the industrial eucalypt chips*.

Mg (ppm)	Cu (ppm)	Fe (ppm)	Mn (ppm)
124.9	0.74	8.90	54.9

* ppm on o.d. wood.

PHOSPHONATES ADDITION IN PULPING AND BROWN STOCK WASHING

DTPMPA

Pulping results and pulp metal ion contents, after DTPMPA addition in pulping and brown stock washing, are shown in Table 4.

There were no statistical differences in yield, rejects, COD, Kappa number and viscosity between the different runs under the same conditions.

Precision of metal ion determinations, using atomic absorption spectrometry, was 33% for Cu, 2.1 ppm for Fe, and 21% for Mn (TAPPI T266 om-94).

The experimental data was analysed by Analysis of Variance as shown in Table 5. Ion determination errors include variations in the analytical results; runs include repetitions of pulping and brown stock washing, and represent errors due to pulp manipulation and raw material variation.

As copper values were all below 0.5 ppm, the comparison of differences with errors is not significant. The same conclusions are valid for iron. There are no precision values reported for magnesium, but it was clearly not affected by any treatment. The applied treatments influenced only Mn (96% of variation).

Manganese reduction in pulps is due to DTPMPA incorporation in brown stock washing, and in both stages.

Copper and iron present an unexpected effect. They increase when adding DTPMPA in cooking and in brown stock washing.

Table 4
Pulping results and metal ion content using DTPMPA in cooking and brown stock washing*.

Treatment	Total Q dosage	Unscreened pulp yield	Screened pulp yield	Rejects	Viscosity	Kappa number	COD	Mg	Cu	Fe	Mn
	%	%	%	%	cp		kg/t	ppm	ppm	ppm	ppm
1. Control	0.0	50.5	50.2	0.34	47.7	16.1	0.76	29	0.26	4.47	6.82
2. DTPMPA	0.1	50.9	50.8	0.27	46.3	15.7	0.73	28	0.33	3.74	1.42
3. DTPMPA	0.2	50.8	50.7	0.12	47.4	16.0	0.76	27	0.29	3.44	2.84
4. DTPMPA	0.3	51.0	50.9	0.13	47.9	15.9	0.73	29	0.48	7.45	0.76

* All percentages are based on o.d. pulp or wood as appropriate.

Table 5
Variance components analysis for metal ions (DTPMPA).

Source of variation	Variance component %			
	Mg	Cu	Fe	Mn
Count	21	24	36	36
Treatment	9.1	18.2	7.9	96.0
Run	15.5	77.0	55.8	3.8
Ion determination	43.9	1.8	30.8	0.0
Unexplained error	31.4	3.0	5.5	0.1

Release of metal ions from the equipment could be the reason for this.

Pulp properties are shown in Table 6.

Bulk was not affected by DTPMPA addition in pulping, but adding chelant in brown stock washing (treatment 2) gave a significant decrease in bulk. DTPMPA present in pulping or washing did not have any affect on tear index, while both treatments increased burst index. Tensile index reacted the same way, but the increases were small.

Brightness increased with DTPMPA addition in cooking but not in brown stock washing. Colour parameter L* behaved as with brightness, while a* (red tendency) showed an opposite behaviour, and b* (yellow trend) decreased slightly using treatment 2.

Air resistance behaved similarly to density, and opacity to bulk.

SPAP

Pulping results and metal ions content with SPAP addition are shown in Table 7.

Pulps were not statistically different in yield, rejects and COD, but SPAP addition in cooking increased pulp viscosity.

Manganese behaviour was similar to that for DTPMPA. Treatment 4 exhibited the best values, followed by treatment 2.

Adding SPAP in the white liquor preserved the Mg content in pulp. SPAP is more effective than DTPMPA in iron reduction and in magnesium preservation, and gave the highest viscosity levels.

Concerning Cu, SPAP performed in a similar way to DTPMPA. It had a negative effect on Cu and Fe when added in cooking, but not in brown stock washing.

Pulp properties are shown in Table 8.

SPAP addition in brown stock washing did not affect bulk, but bulk decreased when SPAP was introduced in the white liquor. Burst index reacted in the opposite way, and so did tear index, brightness and colour parameter L*.

Colour parameters a* and b* were negatively affected by the presence of SPAP in washing waters (treatment 2), but they showed inferior levels when SPAP was applied only in cooking (treatment 3).

Tensile index seemed to behave in the same way as burst, but differences were small compared to the standard errors. Once again, air resistance behaved similarly to density, and opacity to bulk.

Generally, all properties were not affected when SPAP was applied in brown stock washing (treatments 2 and 4), but they improved when SPAP was used in cooking (treatment 3).

CHELANT ADDITION DURING WASHING

Table 9 and Figures 1 and 2 show results for pulps washed with different chelating agents.

Viscosity variations were not significant for the various treatments (Fig. 1). When washing with acid, the carryover lignin clearly precipitated onto fibres causing a significant increase in Kappa number. COD values clearly show that organic matter remains in the pulp, and therefore washing became less efficient (Fig. 2). This effect is clearly deleterious to the following oxygen stage.

Even though the acidity required in the EDTA stage was not particularly low (pH = 5.5), Kappa number and COD of this treatment are similar to those produced in the strong acid stage.

Figure 3 shows the levels of Mg and Mn ions achieved in the treated and untreated pulps.

The Analysis of Variance (Table 5) showed there were significant differences between treatments. Multiple range tests showed that DTPMPA and SPAP treatments gave similar reductions in Mn content, reducing it to a very low level immediately after the pulping stage. However, Mn levels after HEDP addition in brown stock washing were little affected and were similar to the control (Fig. 3). Acid treatment and EDTA produced the greatest Mn reduction.

EDTA preserved the best levels of Mg (which is a protector in the O stage), followed by DTPMPA, HEDP, SPAP and the control, while strong acid treatment eliminated almost all Mg.

Cu concentrations were generally low, and there were no significant differences between treatments. All the chelants produced similar reductions in Fe levels.

Pulp physical properties are shown in Table 10 and Figures 4 and 5.

Acid, EDTA, DTPMPA and SPAP treatments produced lower tensile index and higher tear index than the control.

Figure 5 shows that both acidic treatments produce yellowish pulps with the lowest brightness values.

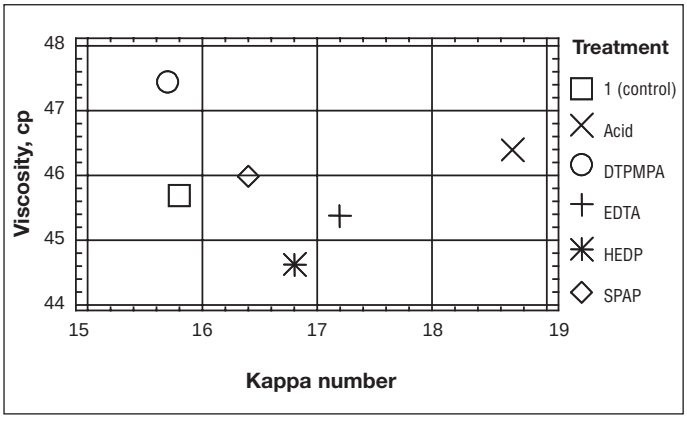

Fig. 1 Viscosity vs. Kappa number for chelant addition in brown stock washing.

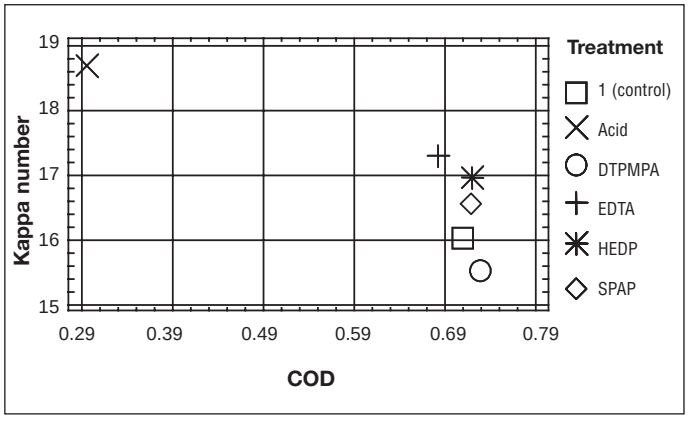

Fig. 2 Kappa number vs. COD for chelant addition in brown stock washing.

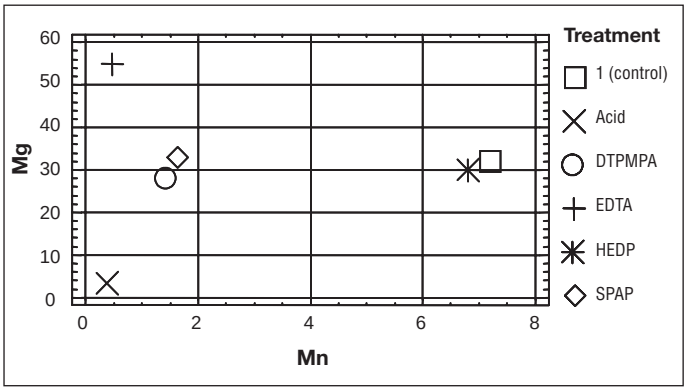

Fig. 3 Pulp Mg vs. Mn content for chelant addition in brown stock washing.

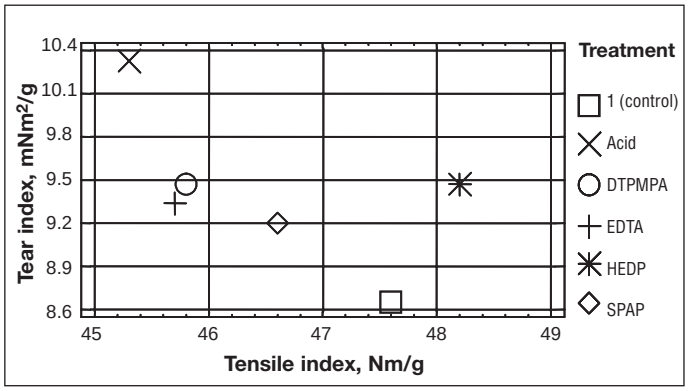

Fig. 4 Tear index vs. tensile index for chelant addition in brown stock washing.

CONCLUSIONS

Adding phosphonates in cooking or in brown stock washing is a valid option for removal of harmful ions before the oxygen stage. This option involves the use of new phosphonate products that perform successfully under high temperature and pH conditions.

DTPMPA addition in cooking and in brown stock washing reduced Mn to a very low level, preserving or increasing pulp physical properties compared to the control (pulping or washing without chelants).

SPAP increased pulp physical properties when applied only in cooking, but it performed best with metals removal when dosed in brown stock washing.

In both cases, Mn levels after 0.1% DTPMPA or SPAP addition in brown stock washing were reduced to below 2 ppm without the use of a separate Q stage.

Even though an acidic washing at pH = 2 produced a beneficial reduction in ions, concomitant lignin precipitation onto fibres would make this operation unviable. Washing efficiency would be reduced, revealed by an increase in Kappa number and reduction in COD, which would adversely affect the following oxygen stage.

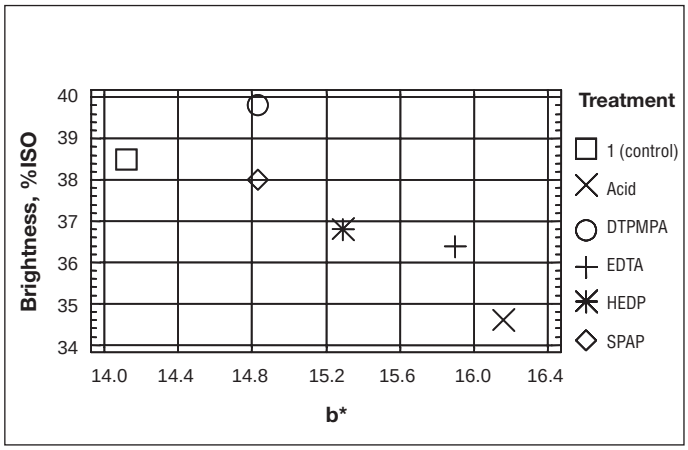

Fig. 5 Brightness vs. b* for chelant addition in brown stock washing.

Table 6
Pulp properties using DTPMPA in pulping and brown stock washing.

Treatment	Bulk	Tear index	Tensile index	Burst index	Air resistance	Brightness	L*	a*	b*	Opacity
	cm³/g	mNm²/g	Nm/g	kPam²/g	s	% ISO				%
1. Control	1.813	7.13	36.4	1.67	2.46	43.2	80.0	2.62	14.65	98.6
2. DTPMPA	1.693	7.38	37.0	1.98	3.43	43.3	79.7	2.54	14.06	98.1
3. DTPMPA	1.805	7.14	37.5	1.84	2.50	44.1	80.5	2.42	14.49	98.6
4. DTPMPA	1.754	7.12	38.2	2.03	2.94	42.5	79.5	2.51	14.60	98.2

Table 7
Pulping results using SPAP in pulping and in brown stock washing*.

Treatment	Total Q dosage	Unscreened pulp yield	Screened pulp yield	Rejects	Viscosity	Kappa number	COD	Mg	Cu	Fe	Mn
	%	%	%	%	cp		kg/t	ppm	ppm	ppm	ppm
1. Control	0.0	50.5	49.8	0.78	45.7	16.0	0.72	43	0.26	3.42	9.43
2. SPAP	0.08	50.9	49.8	0.78	44.7	16.7	0.69	33	0.38	1.87	1.99
3. SPAP	0.2	50.7	50.2	0.47	52.3	16.4	0.81	69	0.75	7.96	3.86
4. SPAP	0.3	50.7	50.2	0.47	53.8	17.3	0.67	51	0.23	5.81	1.11

* All percentages are based on o.d. pulp or wood as appropriate.

Table 8
Pulp properties using SPAP in pulping and in brown stock washing.

Treatment	Bulk	Tear index	Tensile index	Burst index	Air resistance	Brightness	L*	a*	b*	Opacity
	cm^3/g	mNm^2/g	Nm/g	$kPam^2/g$	s	% ISO				%
1. Control	1.59	9.10	47.6	2.92	3.00	38.5	76.4	2.92	14.12	98.7
2. SPAP	1.58	9.30	47.3	2.93	3.23	38.7	77.4	3.11	15.59	98.9
3. SPAP	1.50	10.1	48.3	3.15	4.63	43.2	79.7	2.77	14.21	98.6
4. SPAP	1.56	8.78	47.2	2.95	3.48	40.0	78.4	3.10	15.78	98.7

Table 9
Pulp properties using different chelating agents in brown stock washing.
(Q = 0.1% on o.d. pulp)

Treatment	Chelant addition*	Viscosity	Kappa number	COD	Mg	Cu	Fe	Mn
		cp		kg/t	ppm	ppm	ppm	ppm
1. Control	–	45.7	16.0	0.71	32	0.38	4.32	7.20
2. Acid	***	46.4	18.7	0.30	3.4	0.29	2.72	0.37
2. DTPMPA	0.1	47.4	15.8	0.73	28	0.30	3.74	1.42
2. EDTA	0.1**	45.4	17.6	0.68	55	0.18	2.27	0.46
2. HEDP	0.1	44.7	17.0	0.72	30	0.40	2.40	6.81
2. SPAP	0.1	46.0	16.6	0.72	33	0.32	2.41	1.63

* % active acid base on o.d. pulp.
** + H_2SO_4 to pH = 5.5
*** H_2SO_4 to pH = 2

Table 10
Properties of pulps using different agents in brown stock washing.
(Q = 0.1% on o.d. pulp)

Treatment	Bulk	Tear index	Tensile index	Burst index	Air resistance	Brightness	L*	a*	b*	Opacity
	cm^3/g	mNm^2/g	Nm/g	$kPam^2/g$	s	% ISO				%
1. Control	1.59	8.65	47.6	2.92	3.00	38.5	76.4	2.92	14.12	98.7
2. Acid	1.59	10.3	45.3	2.86	3.34	34.6	74.6	3.17	16.16	98.8
2. DTPMPA	1.56	9.47	45.8	2.87	3.71	39.8	77.7	2.77	14.83	98.1
2. EDTA	1.71	9.34	45.7	2.64	2.74	36.4	75.8	3.22	15.90	99.2
2. HEDP	1.68	9.47	48.2	3.00	3.10	36.8	75.8	3.09	15.29	99.1
2. SPAP	1.67	9.20	46.6	2.92	3.08	38.0	76.4	2.93	14.83	98.9

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