

Phosphonates as additives in kraft pulping—a preliminary investigation

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ABSTRACT: The performance of phosphonates as additives in kraft pulping of aspen was investigated. Application of 0.1%-0.2% phosphonates in cooking resulted in considerable reduction in kappa number (4-8 points), while pulp yield was increased substantially. The bleaching responses of phosphonate treated pulps to DEDED and OPD sequences were significantly improved, allowing lower chemical application or higher final brightness. In addition to enhanced lignin removal, the improved bleachability is likely extended by an appreciable decrease in metal content of pulp fibers.

Application: Kraft mills may be able to apply phosphonates as additives in the digester to achieve higher yield, shorter cooking times and better bleaching response.

As the predominant pulping technology worldwide for producing chemical pulps of high strength, the kraft or sulfate process contributed to approximately 82.9% of the total pulp production in the United States in 1997, up from 80.4% in 1987 and 48.7% in 1967 [1, 2]. Nevertheless, it is interesting that the process itself has essentially changed little from using HS and OH as active pulping components in the past 50 years. Any effort to improve kraft pulping yield, pulp bleachability, or strength properties could have an important impact on the paper industry. So far, additives such as polysulfides and anthraquinone (AQ) have been commercially used with optimal charge of AQ being around 0.1% [3-4]. AQ is extensively used in Japan, but was accepted in North American only in the 1990s. The major problem reported with the use of AQ—besides the cost—is the formation of deposits in the metering pump, evaporators, and heat exchangers due to low solubility [5].

Phosphonates are usually in the form of an acid or salt with highly anionic charges, containing at least one functional group, $-P(=O)(OH)_2$, attached to a carbon atom. Their complex structures are characterized by phosphoryl bonds and multiple metal ion chelating sites (Fig. 1) for diethylenetriamine pentamethylenephosphonic acid (DTMPA) [6]. Phosphonates are soluble and stable in aqueous systems to high temperatures, pressures, and pH extremes, hence they have many desirable properties such as scale inhibition, sequestration and dispersion. For instance, phosphonates are commonly used for preventing scale buildup in water treatment [7].

Phosphonates have been used as sequesters for metal ion control in peroxide bleaching [8-9]. In this study, we address the potential use of phosphonates during kraft cooking, considering the fact that phosphonates have surfactant properties they should facilitate penetration of chemicals into chips and removal of dissolved lignin from chips. In addition, their chelating properties should favor brightness improvements in subsequent bleaching processes. We studied a wide variety of phosphonates, but will focus here on the responses of hydroxyethylidene diphosphonic acid (HEDP) and DTMPA.

EXPERIMENTAL

We used commercial aspen (*Populus tremula*) chips of about 50% moisture content from Potlatch Corporation (Cloquet, Minnesota, USA) throughout this study. Phosphonates were provided by Solutia Inc. (St. Louis, Missouri). AQ was purchased from Aldrich Chemical Company.

The chips were screened using a 0.25-in. slot screen and sorted by hand to remove knots and bark. Cooking was carried out on a scale of 350 o.d. gram chips with an M/K lab digester under conditions of 18% active alkali (as Na_2O), 25% sulfidity (as Na_2O), liquid-to-chip ratio 4:1, and a maximum temperature of 170°C. We computed all additive charges on the basis of o.d. weight of chips.

D, O, P, and E denote bleaching stages of chlorine dioxide (ClO_2), oxygen (O_2), hydrogen peroxide (H_2O_2), and alkaline extraction, respectively. Each stage was run with at least 60 o.d. gram pulps at 10% consistency with all chemical

charges based on o.d. pulp. The oxygen pressures in O stages were 90 psi. 0.1% $MgSO_4$ was added in O stages, and 0.1% $MgSO_4$ plus 1.5% silicate were charged in P stages. We used plastic bags for D, P, and E stages, and a Mark IV mixer (Quantum Technology) for O stages. Table I lists the other routine conditions used in this work.

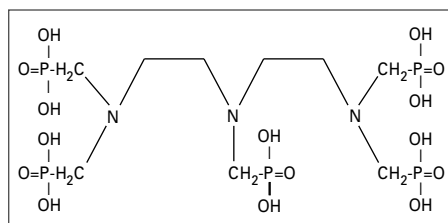
Screened pulp yields and rejects were determined by screening disintegrated pulps on a laboratory screen with 0.015-in. slots. The pulp retained on 200-mesh wire was collected as screened pulp and the residue on the screen as rejects. Yield and rejects were reported as percentages of o.d. chips. TAPPI methods [10] were adopted for other pulp tests such as kappa number [T236 cm-85], pulp CED viscosity [T230 om-94], and pulp brightness [T452 om-92]. Metals on pulp fibers were determined by inductively coupled plasma technique [ARL 3560 ICP-AES].

RESULTS AND DISCUSSION

Effect on kappa number

Industry and laboratories routinely use the kappa number, an indirect means of measuring residual lignin, to represent relative hardness, degree of delignification, or bleachability of chemical pulps below 70% pulping yield. Thus, the effect of phosphonates on pulp kappa number is our primary consideration in this study. The experimental results applying HEDP and DTMPA as additives to conventional kraft cooking are given in Table II, along with AQ modified pulps and the control as references.

The experiment was set up as a factorial design with two factors: the H-factor at four levels, and the other, the treat-



1. Structural formula for DTMPA.

STAGE:	D	O	P	E
Temperature (°C)	70	90	85-87	70
Retention time (min)	90	45	120	60
NaOH applied (%)	*	2.5	2.0	2.0

* 0.2% NaOH was applied for each 1% ClO₂ applied in D stages.

I. Routine conditions used in this study.

ments at five levels (Table II). We then applied statistical analysis using MacAnova [11]. Results demonstrate that 0.1%-0.2% addition of either HEDP or DTMPA give rise to significant reduction in kappa number varying from 4.2 to 7.9 points in the entire H-factor range studied, i.e. 558 to 1000, indicating that delignification is dramatically improved by phosphonate addition. The lower the applied H-factor, the greater is the reduction. Analysis also implies that 0.1% HEDP, 0.2% DTMPA, and 0.1% AQ are equivalent in terms of delignification, whereas 0.2% HEDP resulted in further kappa number reduction by 1-3 points.

Pulps cooked with 0.1%-0.2% phosphonates at H-factor 600 are comparable in kappa number to pulps processed without additive at H-factor 1000. In other words, for a target kappa number (e.g. 21) at the fixed H-factor 1000, application of 0.1%-0.2% phosphonates would mean a 27 min. savings in total cooking time (Fig. 2). This would certainly result in significant savings in operating costs while increasing productivity.

Effect of phosphonate charges

Impacts of phosphonate charges as well as its optimal dosage were investigated using HEDP. Table III lists the effects of HEDP addition on pulp properties.

Kappa number drops from 24.5 without HEDP addition to 14.8 with 0.4% HEDP charge (Fig. 3). There is a steep drop in kappa number between the 0% and 0.05% addition levels, while the points for 0.05%-0.4% are on a fairly straight line with a much lower slope. This might mean that there could be two different regimes for phosphate action.

The largest increase in brightness was measured as high as 9 points. The initial pulp brightness increases consistently as HEDP charge increases but the trend appears to slow down when the charge reaches 0.2%-0.3% (Fig. 4). Considering the efficiency/cost ratio simultaneously, 0.1%-0.2% was determined as the optimal charge of HEDP in this study.

Effects on pulp yield and rejects

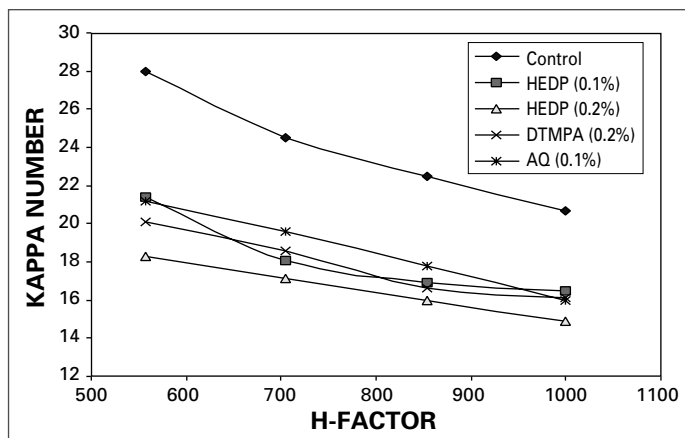
In industrial practice, at desired lignin removal levels, pulp yield is of great interest to pulp producers as it is directly associated with production and thus profitability. AQ is reported to improve pulp yield by 1%-3% through stabilizing carbohydrates against alkaline degradation [12-13]. Results in Figs. 5 and 6 show that 0.2% HEDP improve screened pulp yield by 1%-5% at H-factors over 600. In addition, the reject level is reduced by 0.5%-5% at H-factors below 800. The performance of AQ is comparable in both aspects. The gain in yield and decrease in rejects are particularly noticeable at low H-factors, i.e. <700, but gradually become negligible at high H-factors, i.e. >900. The outcome of low rejects was most likely due to improved delignification. HEDP addition led to reduced rejects especially at low H-factor, which partially contributed to higher screened yield.

KAPPA NUMBER H-factor	TREATMENTS				
	CONTROL	HEDP (0.1%)	HEDP (0.2%)	DTMPA (0.2%)	AQ (0.1%)
558	28.0	21.4	18.3	20.1	21.2
705	24.5	18.1	17.1	18.6	19.6
853	22.5	16.9	16.0	16.6	17.8
1000	20.7	16.5	14.9	16.1	16.0

II. Effect of phosphonates on kappa number at different H-factors.

HEDP CHARGE, %	KAPPA NUMBER	SCREENED YIELD, %	VISCOSITY, CP	INITIAL ISO BRIGHTNESS, %
0.00	24.5	51.2	45.4	28.2
0.05	19.1	52.8	42.2	32.4
0.10	18.1	53.7	42.7	33.1
0.20	17.1	53.9	43.1	35.2
0.30	15.7	53.1	43.3	36.2
0.40	14.8	53.2	43.0	37.1

III. Effect of HEDP charge at fixed H-factor 705.



2. Effect on kappa number.

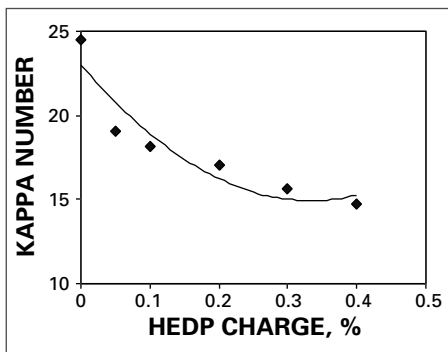
Therefore, it is helpful to consider the total recovered material, i.e. the sum of the screened pulp and the rejects. Figure 7 shows that at a given Kappa number the total recovered material is considerably higher for the HEDP treated sample compared to the control. The AQ sample, even though around 3% higher than the control, is inferior to the HEDP pulps.

Trials related to this work performed at Potlatch Fiber R&D Center in January 2001 were consistent with the results on yield presented here. The observed improvements in total yield were 1.3% to 4.5% at H-factors 600 through 1200 for 0.2% HEDP. The result also can be justified by recent carbohydrate analysis using gas chromatography, which will be presented elsewhere.

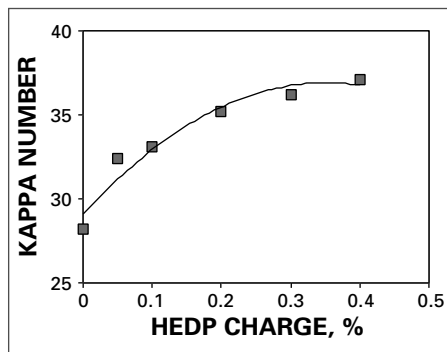
Effect on pulp viscosity

Measuring the degree of cellulose polymerization (DP), pulp viscosity is an important parameter monitoring the extent of carbohydrate degradation during pulping and is generally considered an indicator of pulp strength properties. According to Table III, absolute pulp CED viscosity values at given H-factors are

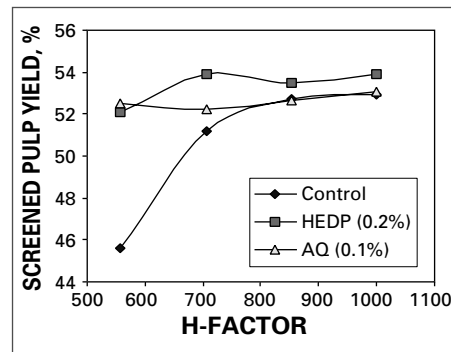
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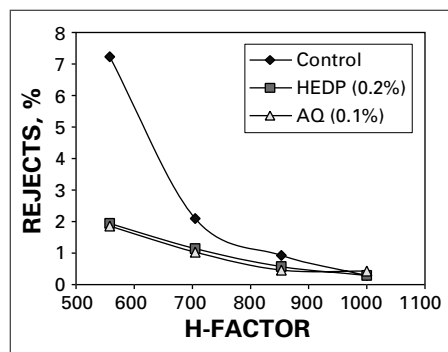
3. Effect of HEDP charges—kappa number v. charge.



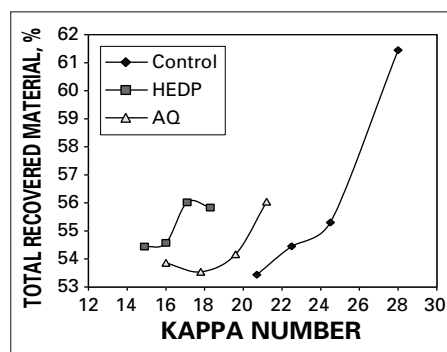
4. Effect of HEDP charges—pulp brightness v. charge.



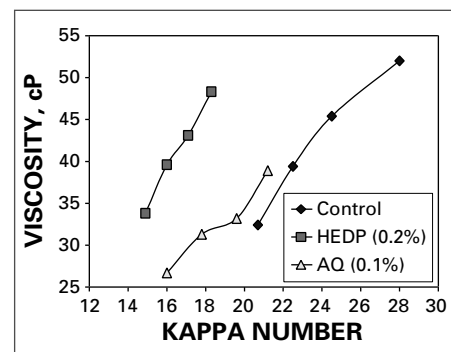
5. Effects on pulp yield—screened pulp yield v. H-factor.



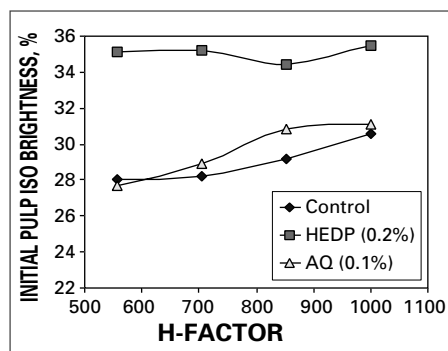
6. Effects on rejects—rejects v. H-factor.



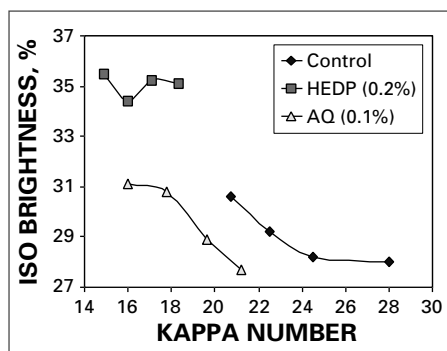
7. Effects on pulp yield—total recovered yield v. kappa number.



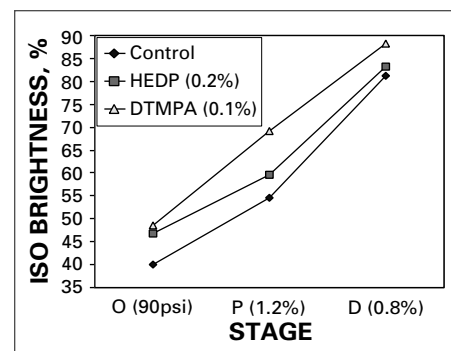
8. Effect on pulp viscosity.



9. Effect on initial pulp brightness—initial pulp brightness v. H-factor.



10. Effect on initial pulp brightness—brightness v. kappa number.



11. Brightness responses to OPD sequence.

Note: (1) Initial ISO brightness (%): Control 28.3, HEDP (0.2%) 35.2, DTMPA (0.2%) 33.8; (2) Initial viscosity (cP): Control 45.4, HEDP (0.2%) 43.1, DTMPA (0.2%) 38.5

slightly decreased (2-3 centipoises) by HEDP addition. However, comparisons made at equivalent degree of delignification (Fig. 8) reveal that HEDP treated pulps actually show considerable increases with respect to pulp viscosity. Use of AQ resulted in similar viscosity improvement, but the difference to the control is significantly less.

Effect on pulp brightness

The influence of phosphonates on initial pulp brightness is another interesting outcome of this research. All pulps were well-washed with tap water before brightness determination in order to

minimize variability in operation. Figure 9 illustrates that HEDP modified pulps have considerably higher brightness than control pulps at all H-factors. The improvement is consistently 5-7 points. AQ application gives rise to brightness values similar to the control at given H-factors. Still, if compared at a given kappa number AQ modified pulps actually showed a lower brightness than the control (Fig. 10).

Moreover, the relationship between pulp brightness and kappa number (Fig. 10) indicates that the pulp brightness of either AQ-modified pulps or the control

is generally constrained to 27%-31% ISO. In contrast, HEDP-treated pulps consistently reach 35% ISO, 4-8 points higher. It is implied that in addition to residual lignin content, other fundamental features of HEDP treatment contribute to the brightness. One explanation would be the formation of chromophore structures in lignin has been limited by phosphonate addition. Another proposed factor might be reduced metal content on fibers.

Metal contents on fibers

Prominent metals on pulp fibers include Na, Ca, Mg, Mn, Cu, Fe, Zn, and Al, which are often introduced by woodchip and process chemicals/water. Of great concern are transition metals such as Mn, Cu, Fe, etc. as well as alkaline earth metals (Ca and Mg). The former interfere with activities of oxidizing agents (e.g., O_2 , H_2O_2) in pulp bleaching and the latter can cause serious scaling problems in the process. Thanks to the ionization of carboxylic acids and phenolic groups, pulp fibers are usually charged negatively and can, as a result, act as ion exchangers. For example, carboxyl groups present as hexeneuronic acid on xylan structures [14-15] have a strong affinity for metal ions. Ion exchange capability of kraft pulps has been discussed in literature [16, 17]. An issue of particular interest for this study is the effect of phosphonates on metal contents of pulp fibers. For this purpose, four pulps, i.e., 0.2% HEDP, 0.2% DTMPA, 0.1% AQ and the control were thoroughly washed with tap water ahead of metal determination by ICP method. **Table IV** shows the results.

We again applied MacAnova for data analysis. We concluded that DTMPA is effective for removing cations such as Ca, Mn, Cu, and Zn, with removal rates up to 27%, 60%, 38%, and 42%, respectively. HEDP tends to reduce Ca as well, but the effect is not statistically significant. As expected, AQ shows no effect on metal removal at all. HEDP or DTMPA demonstrated little effect dealing with iron, whereas the Mg content, accounting for 10% of the total metals on fibers, increased by 15% on any phosphonate application. On the other hand, concentrations of such transition metals as Cu, Fe, and Mn are too low (roughly 1-14 ppm) to completely explain the brightness changes observed for the HEDP-treated pulps. As proposed earlier, some additional effect other than metal removal might be involved simultaneously.

Bleaching responses

We evaluated two bleaching sequences (DEDED and OPD) for phosphonate-modified pulps in this work. No additional phosphonate was added to any of the actual bleaching stages.

PULPS	METAL CONTENTS, PPM						
	CA	MG	ZN	AL	CU	FE	MN
Control:	2338.3 (143.4)	241.8 (25.5)	34.9 (7.45)	15.2 (4.52)	14.0 (1.65)	11.1 (2.42)	2.7 (0.49)
HEDP(0.2%):	2127.3 (98.2)	275.2 (12.2)	29.4 (10.97)	16.6 (2.27)	11.4 (1.40)	10.2 (1.47)	3.1 (0.83)
DTMPA(0.2%):	1706.5 (48.5)	279.3 (9.2)	20.4 (3.27)	13.3 (1.85)	8.60 (1.72)	15.9 (7.07)	1.0 (0.16)
AQ(0.1%):	2588.4 (263.0)	241.4 (18.7)	23.0 (4.98)	17.1 (1.32)	12.0 (3.47)	10.1 (1.73)	3.2 (0.19)

Averages of four replicates taken at four H-factors. (Standard Deviation) shown in parenthesis.

IV. Metal contents on various pulp fibers.

	CONTROL	HEDP (0.2%)	DTMPA (0.2%)	AQ (0.1%)
Initial kappa number	22.5	16.0	18.6	17.8
Initial ISO brightness, %	29.2	34.4	33.7	30.8
Total ClO_2 charge, %	2.0	1.6	1.7	1.7
D0: ClO_2 , %	1.3	1.0	1.0	1.0
ISO brightness, %	44.8	53.7	53.7	55.5
E1: ISO brightness, %	57.7	62.0	62.2	63.1
D1: ClO_2 , %	0.5	0.4	0.5	0.5
ISO brightness, %	83.3	84.1	84.8	85.1
E2: ISO brightness, %	82.6	83.4	84.5	84.9
D2: ClO_2 , %	0.2	0.2	0.2	0.2
Final ISO brightness, %	90.5	90.6	90.7	90.7

V. Brightness responses to DEDED sequence.

DEDED sequence

We slightly varied total ClO_2 charge in an attempt to demonstrate the total ClO_2 charge needed to reach a given brightness. **Table V** presents the brightness responses.

Brightness improvements for HEDP and DTMPA treated pulps in D_0 and E_1 stages are significant. In the D_0 stage, treated pulps obtain an increase of approximately 20 points using 1% ClO_2 , 4 points higher than the control with 1.3% ClO_2 charge. AQ modified pulps behave similar to DTMPA or HEDP treated pulps, yielding considerable brightness improvement in D_0 and E_1 stages. Considering the variations in initial brightness it becomes apparent that the initial kappa number instead of initial brightness played a principal role in bleaching response. HEDP treated pulp can achieve a brightness over 90% ISO with 0.4% less ClO_2 charge than the control.

OPD sequence

Figure 11 shows that the improvements in brightness of HEDP and DTMPA treated pulps are significant, especially in O

and P stages. In addition, the DTMPA treated pulps demonstrate a better performance than the HEDP treated pulp. Specifically, the brightness gain obtained by DTMPA modified pulp in the O stage is 14.5 points, 3.5 points higher than the control. In the subsequent P stage, the accumulated brightness advantage for the DTMPA treated pulp is nearly 10 points, while the HEDP treated pulp shows a relatively smaller brightness rise in the O and P stages.

Subjected to identical bleach chemical charges, the control, HEDP and DTMPA treated pulps end up with brightness values of 81.3%, 83.1%, and 88.3% ISO respectively, with corresponding kappa numbers dropping from 24.5, 17.1, and 16.6 to 10.8, 8.9, and 6.9. Apparently, the control pulp would need additional bleaching agent(s) to achieve the same high brightness values. The superiority of phosphonate-modified pulp in brightness responses might be explained in part by the metal removal effect, as discussed in the previous section. On the other hand, HEDP modified pulps show a higher viscosity than the

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control at the end of the O stage (35.2 vs. 34.3 centipoises). They maintain the small advantage through the subsequent bleaching stages (27.8 vs. 26.7 centipoises).

CONCLUSIONS

This study demonstrates that phosphonates are efficient additives in kraft pulping of aspen. Addition of 0.1%-0.2% HEDP or DTPMA resulted in greatly enhanced delignification, which was demonstrated by a reduction in kappa number of 5.5 points on average. Extended lignin removal and pulping uniformity led to remarkable decrease in rejects especially at low H-factors. Pulping yield significantly improved, even at reduced kappa number. Application of HEDP or DTPMA in the digester yields pulps of higher initial brightness and viscosity at given degrees of delignification or pulps of comparable kappa number with much shorter cooking cycle time.

Phosphonate treated pulps display improved responses to subsequent bleaching sequences such as DEDED and OPD, allowing ClO₂ minimization without compromising high target brightness. Beyond extended lignin removal, a measurable decrease in metal ions of pulps including Mn and Cu is likely to be responsible for the enhanced bleaching performance.

Evidently, addition of phosphonates in hardwood kraft cooking significantly improves pulp properties and the overall performance in bleaching processes, offering a feasible substitute for pulping additives including AQ. **TJ**

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INSIGHTS FROM THE AUTHORS

Why did you choose this topic to research?

Kraft cooking is a very common process, and improvements have the potential to result in large cost savings. We originally were hoping for increased bleachability and bleaching chemical savings due to metal removal.

How does this research either compliment or differ from previous research?

This is an entirely new approach.

What was the most difficult aspect of this research and how did you address that?

This research is still in its preliminary stage. One of the main issues is the fact that the effect of phosphonates apparently is species sensitive. At this point we are screening different wood species and continue work on the fundamental mechanism involved in these reactions.

What did you personally discover from this research? What was most interesting or surprising about your findings?

The results exceeded our original expectations. We did expect changes in bleachability, but did not expect the substantial yield increases observed.

How might mills benefit from or use this information?

Obviously yield increase in kraft cooking is of great interest for mills. In addition, this project has the potential for energy savings and savings in bleaching chemicals.

What's the next step?

At present, we are working with different wood species and are analyzing pulp and black liquor samples to understand fundamental mechanism involved in the phosphonate actions. In addition, we

are investigating the fate of the phosphonates in the kraft recovery cycle.

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