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POTENTIAL USES FOR PEROXYMONOSULFATE IN PULPING AND BLEACHING

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ABSTRACT

Practical and cost-effective uses for peroxymonosulfate can be developed in pulping and bleaching. Peroxymonosulfate pulping produces strong pulps, has lower capital requirements, and is less environmentally troublesome compared with current pulping processes. The cost of oxidant may, however, be somewhat too high for practical use. We discuss means for reducing the cost and for disposal or recovery of the spent treating liquors. Low-lignin chemical pulps were effectively bleached by alkaline solutions of peroxymonosulfate. Our results indicate that a practical bleaching sequence can probably be developed employing only peroxymonosulfate and oxygen as oxidizing agents.

KEYWORDS: Peroxymonosulfuric acid, hydrogen peroxide, sulfuric acid, aspen, pulping, bleaching

INTRODUCTION

Current industrial processes for pulping wood and annual plants and for bleaching the resultant pulp have evolved slowly over many decades. Although these processes are quite complex and energy-intensive, they are fairly efficient. Their major disadvantage is their negative impact on the environment. Even the best of current technology is unable to completely suppress the odors emitted by kraft pulp mills or to completely eliminate the emission of chlorinated organic compounds from waste treatment plants associated with pulp mill bleach plants. The discovery of new methods for more easily or more effectively delignifying wood could lead to the development of new, more efficient, less environmentally troublesome pulping and bleaching processes.

A few years ago, we began studying the possibility of using inorganic peroxides for delignification. Organic peroxides, such as peracetic and performic acids, readily delignify wood and other lignocellulosic materials (1). With the exception of studies using alkaline hydrogen peroxide, few, if any, studies have addressed delignification with inorganic peroxides. Alkaline hydrogen peroxide can remove some lignin from lignocelluloses but, in general, it is quite ineffective in delignification. Recently, we found that dilute aqueous solutions of the peroxymonosulfate anion, under mildly acidic conditions and at low temperature (20°C-50°C) and atmospheric pressure, are very effective in delignification of wood (2). The peroxymonosulfate treatment must be followed by an alkaline extraction to solubilize and remove the fragments of depolymerized lignin. Some representative data on delignification of finely divided aspen wood using the peroxymonosulfate anion are given in Table 1. Peroxymonosulfuric acid can be easily produced by mixing concentrated hydrogen peroxide with concentrated sulfuric acid. A triple salt containing potassium peroxymonosulfate is sold under the trade names Oxone and Curox (or KMPS) by E.I. Dupont de Nemours and Company (Wilmington, DE) and by Interox America (Houston, TX).[2]

The discovery of the delignifying ability of mildly acidic peroxymonosulfate solutions led to a consideration of the potential end-uses for these solutions in pulping and bleaching. Such solutions might be used to treat wood or other lignocellulosics to produce chemical-type pulps or to treat mechanical, thermomechanical, chemimechanical, or chemithermomechanical pulps to improve their strength properties. These solutions might be used to restore or improve the strength of secondary fiber from unbleached softwood kraft wastepaper, old corrugated containers, or old newsprint. Peroxymonosulfate might also be used as a replacement for chlorine and chlorine dioxide in pulp bleaching or as a pretreatment prior to oxygen bleaching. These end-uses require thorough and careful evaluation. The objective of this report was to review research to date on these end-uses and to indicate promising areas for future work. It seems highly probable that practical, cost-effective uses for peroxymonosulfate can be developed in the areas of pulping and bleaching.

DELIGNIFICATION OF LIGNOCELLULOSES

To determine the most economically promising applications for peroxymonosulfate, data were taken on the consumption of peroxymonosulfate required to attain low lignin levels in various types of lignocelluloses. Dilute solutions of Oxone were applied to finely divided (particle size <0.42 mm (40 mesh)) aspen wood, spruce wood, and oat straw and to a bleachable-grade spruce kraft pulp and a Douglas-fir linerboard pulp. After reaction for various periods at room temperature, the spent reaction solutions were analyzed for remaining oxidant and the consumption of peroxymonosulfate was calculated. The alkaline-extracted, thoroughly washed residues and the initial untreated lignocelluloses were analyzed for Klason lignin content. The results of these experiments are plotted in Figure 1. The peroxymonosulfate anion contains one atom of active oxygen.

Several conclusions can be drawn from Figure 1. The high values for grams of lignin removed per gram of active oxygen consumed at low grams of lignin removed per gram original substrate indicate that the initial removal of lignin is quite easily accomplished. As more lignin is removed, the removal becomes increasingly difficult; removal of the last traces of lignin is exceedingly difficult. The curves intersect the abscissa

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at the original lignin content of the particular lignocellulose. If the curves were extrapolated back to the ordinate (g lignin removed/g active oxygen consumed), the relative ease of initial lignin removal would be indicated. This order appears to be as follows: Douglas-fir linerboard kraft pulp, oat straw, aspen wood, bleachable spruce kraft pulp, and spruce wood. For spruce wood, even the initial removal of lignin is apparently quite difficult. Because spruce wood contains about 29 percent lignin, delignification to obtain a low-lignin, chemical-type pulp is probably not economically feasible. Chemical-type pulps can be more easily produced from aspen wood and straw because of their lower lignin contents and greater ease of lignin removal. Delignification of linerboard pulps and bleachable-grade softwood kraft pulps also seems to be feasible. These low-lignin substrates would consume much less oxidant. Based on these considerations, we initiated work on production of low-lignin, chemical-type pulps from hardwoods and on bleaching of kraft pulps.

PULPING

Chemical Pulp From Aspen

Initially, we studied the possibility of producing a chemical-type pulp from aspen wood (3). We used fiberized wood because wood chips are not easily penetrated by oxidizing agents, especially under acidic conditions. Hardboard fibers, produced by heating chips to 177°C and then fiberizing them in a disc refiner, were treated with acidic peroxymonosulfate and then extracted with dilute sodium hydroxide. Pulping conditions together with pulp yields and lignin contents are given in Table II. For purposes of comparison, a chlorine dioxide treatment was also used. Handsheet strength data are shown in Figure 2. Data for aspen kraft pulp from chips and for kraft pulping of the hardboard fibers are also shown in Figure 2. Kraft pulping conditions are given in Table III.

The tensile and tear strength values of pulps treated with peroxymonosulfate and chlorine dioxide were somewhat lower than the strength values of kraft pulp from chips. However, the tensile strength values were significantly higher than those for the kraft pulped hardboard fiber. Both tensile and tear strengths for the peroxymonosulfate pulps are sufficiently high for most applications. The peroxymonosulfate pulps also had good compressive properties. These pulps should be usable in corrugated box manufacture in both linerboard and corrugating medium and in such products as printing papers, toweling, tissue, and fluff pulp. As Tables II and III indicate, the yields of the peroxymonosulfate pulps were higher than the yields of the kraft pulps. In addition, the peroxymonosulfate pulps were much easier to bleach than were the kraft pulps. The pulps were readily bleached to nearly 80 percent brightness using only a single stage of alkaline hydrogen peroxide.

Peroxymonosulfate pulping has several attractive advantages: low energy requirements, low temperature and pressure operation, relatively innocuous effluents, relatively low capital requirements, easily bleached pulps, and high pulp yield. Two significant disadvantages are the high cost of peroxymonosulfate and the problem of recovery or disposal of the spent treating and extraction liquors. These disadvantages will have to be overcome before a practical industrial process can be developed.

Reduction of Peroxymonosulfate Cost

If peroxymonosulfuric acid is produced by reacting 70 percent H_2O_2 with concentrated sulfuric acid (about 78 percent yield based on peroxide), about 150 kg of peroxide are required per ton of pulp produced. At the current cost of peroxide (about \$1.30/kg). this amounts to >\$190 per ton of pulp. As a result of this high cost, we conducted research on reducing oxidant consumption.

Small samples of aspen hardboard fiber were delignified with peroxymonosulfuric acid using a range of reaction conditions, and the oxidant consumption was determined for each set of conditions. The reaction conditions employed and the results obtained are given in Table IV. In delignifying the fiber to a given lignin content in the pulp, we assumed that oxidant consumption would vary somewhat with the reaction conditions employed. Although reaction conditions might have had some slight effect, the results showed that obtaining a given lignin content in the pulp generally required a given amount of oxidant (Fig. 3).

Oxidant cost could be reduced if peroxide cost were lowered. Two alternative methods for producing hydrogen peroxide are presently under investigation. First, Dow Chemical Company is studying a new electrolytic method that promises to lower the cost of peroxide (4,5). Second, E. I. du Pont de Nemours and Company is piloting a catalytic method for producing peroxide directly from hydrogen and oxygen (5). Hopefully, one of these methods will be applied on an industrial scale and will lower the cost of peroxide. Another possibility for reducing oxidant cost would be to produce peroxymonosulfuric acid by oxidizing sulfuric acid with a cheaper oxidant than hydrogen peroxide. If an effective catalyst could be found, it might be possible to oxidize sulfuric acid to peroxymonosulfuric acid using air or pure oxygen. Another alternative might be to develop the Berl electrolytic process for simultaneous production of hydrogen peroxide and peroxydisulfate (6,7). Peroxydisulfuric acid is readily hydrolyzed to peroxymonosulfuric acid (8,9). Theoretically, in the Berl process, one molecule of peroxydisulfuric acid and one molecule of hydrogen peroxide are produced when two electrons are transferred.

The direct production of peroxydisulfate by the Berl process led us to examine the possibility of delignification with peroxydisulfate. Dilute aqueous solutions of ammonium and potassium peroxydisulfates were applied to aspen hardboard fiber and held at room temperature for various periods. All but one of the solutions were acidified with sulfuric acid. It is well known that peroxydisulfate anion oxidations proceed very slowly at room temperature even though this ion has a very high redox potential (10). The silver (I) ion and the copper (II) ion have been found to be effective catalysts (10). We therefore experimented with a copper (II) catalyst in two solutions. As with peroxymonosulfate treatment, the treated fiber was extracted with 1.0 percent NaOH at 50°C for 1 h, then thoroughly washed with distilled water and dried overnight at 60°C in a vacuum oven. Acid addition was required for effective delignification and the copper catalyst was essentially ineffective (Table V). The very long reaction times required suggest that the peroxydisulfate was slowly hydrolyzing to peroxymonosulfate, which was the active oxidant. As we have noted, the peroxymonosulfate anion is a very effective oxidizing agent at room temperature. Increasing the temperature would drastically shorten the reaction times. These data indicate that peroxydisulfate could probably be used directly

to delignify lignocelluloses. However, more work is needed to develop a pulping method based on peroxydisulfate. Given sufficient effort, the cost of oxidant can likely be reduced to a reasonable level.

Recovery and Disposal of Spent Treating and Extracting Liquors

Spent treating liquor from peroxymonosulfate pulping would contain a large amount of sulfuric acid together with some degraded lignin fragments and carbohydrate fragments. However, most lignin and carbohydrate fragments would be in the alkaline extraction liquor. As has been suggested for nitric acid pulping, the treating liquor could be recycled back to the treating stage, and reinforced with fresh peroxymonosulfate, several times before disposal. This approach was found feasible for nitric acid pulping (11). After several uses, the liquor could be neutralized with spent extraction liquor.

The question of how to dispose of the spent extraction liquor is more difficult. If the extraction were performed using sodium hydroxide, the spent extraction liquor might be evaporated and burned as in the kraft recovery cycle. However, this process requires multistage evaporators and a recovery furnace, a very large capital expense. If the extraction could be performed using ammonium hydroxide, the spent extraction liquors could be used as fertilizer. This was found to be feasible for nitric acid pulping (12). The nitric acid extraction liquors had no deleterious effects on plant growth and acted as an effective fertilizer. Because sodium hydroxide was used in the extraction stage in all previous studies on peroxymonosulfate pulping, we evaluated the use of ammonium hydroxide in this stage.

Peroxymonosulfate-treated hardboard fiber was extracted with dilute aqueous solutions of ammonium hydroxide. For purposes of comparison, the treated fiber was also extracted with sodium hydroxide. The results of these extractions are shown in Figure 4. The aspen hardboard fiber was treated with a 20-percent solution of Oxone at a 10:1 liquor-to-fiber ratio at room temperature (22°C) for 24 h. The extractions were performed for 1 h at 50°C. Although a higher concentration of ammonium hydroxide is required to attain a given lignin content in the pulp (for about 5 percent lignin, 0.2 percent NaOH compared with 1.6 percent NH_4OH), the use of ammonium hydroxide is feasible. Larger scale tests are required to evaluate the effect of ammonium hydroxide extraction on pulp strength and bleachability. However, ammonium hydroxide extraction had no negative effect on nitric acid pulps and is expected to have no negative effect on peroxymonosulfate pulps.

If ammonium hydroxide were used in the extraction stage and the spent extraction liquor were used as a fertilizer, the peroxymonosulfate pulping method would be low cost and much more environmentally compatible than the kraft process. The method would be even better if pernitric or peroxymonophosphoric acid could be used in place of peroxymonosulfuric acid in the initial treatment stage. The spent extraction liquors mixed with, and thus used to neutralize, the initial treating liquors could be spread on farm fields or in forests. As a result of the excessive oxidant requirements for delignifying spruce and probably other softwoods, the peroxymonosulfate pulping method would be most suitable for hardwoods and nonwood plant fibers such as straw, bagasse, and kenaf. Because no chemical recovery equipment and pressure vessels are needed, the mill should be quite simple and low in capital cost. Given these conditions, the present cost of peroxymonosulfate might not be excessive and the method may be economically viable. A detailed, comprehensive cost estimate should be prepared.

BLEACHING

Because chemical pulps contain only 55 percent lignin, the use of peroxymonosulfate to delignify these pulps should be economically feasible. It might also be possible to brighten or bleach all types of pulps, both chemical and mechanical, with peroxymonosulfate. In preliminary work, we examined this possibility.

Alkaline solutions of potassium peroxymonosulfate (Oxone) were used to brighten groundwood pulps, kraft pulps, and delignified kraft pulps (13). Compared to bleaching with equivalent amounts (equal active oxygen basis) of alkaline hydrogen peroxide, the peroxymonosulfate was less effective for groundwoods and kraft pulps but as effective for delignified pulps containing ≤1 percent lignin. The brightness increase of the various pulps is plotted as a function of pulp lignin content for both alkaline potassium peroxymonosulfate and alkaline hydrogen peroxide bleaching in Figure 5. An active oxygen level of 0.71 percent (on weight of pulp, equivalent to 1.5 percent hydrogen peroxide) was employed for both oxidants. For the delignified pulps, the bleaching conditions employed for peroxymonosulfate were milder than those for hydrogen peroxide, and the viscosities of the bleached pulps were consequently higher. For chemical pulps, an alkaline peroxymonosulfate stage might be used as one of the last stages of bleaching.

No work, other than that reported here, has been published on the use of acidic solutions of peroxymonosulfate to delignify pulps. The possibility of using such solutions to replace the initial chlorination stage should be investigated. Acidic peroxymonosulfate could greatly reduce the quantity of chlorinated organics and of dioxins and dibenzofurans in the bleach plant effluent. Because no halogens would be present in the spent liquor from the initial stage or in the liquor from the following alkaline extraction stage, these liquors could be sent to chemical recovery.

Acidic peroxymonosulfate might also be used to replace the chlorine dioxide stages in bleaching. If both the chlorination stage and the chlorine dioxide stages could be replaced, all the spent liquors from the bleach plant could be sent to chemical recovery and no environmentally troublesome materials would emerge from the bleach plant. The bleach plant is currently the major source of effluents from a bleached kraft pulp mill that require treatment.

PRETREATMENT PRIOR TO BLEACHING

Acidic oxidative pretreatments of unbleached softwood kraft pulps prior to oxygen delignification allowed greater lignin removal in the oxygen stage before serious pulp strength loss occurred (14,15). Oxidizing agents such as chlorine, chlorine dioxide, and nitrogen dioxide have been found to be effective in pretreatment. We are currently evaluating the effectiveness of acidic peroxymonosulfate in pretreatment. The advantages of peroxymonosulfate are that it contains no halogens and that it can be used in solution, unlike nitrogen dioxide. Peroxymonosulfate pretreatment might make it possible to reduce lignin to 1 percent in the subsequent oxygen stage before serious strength loss occurs. If so, it might be possible to bleach kraft

pulps using only oxygen and peroxymonosulfate in the following stages: (a) pretreatment with acidic peroxymonosulfate, (b) oxygen delignification, and (c) alkaline peroxymonosulfate bleaching. Although parts of this sequence have been studied, the complete sequence has not yet been tried.

The use of peroxymonosulfate in bleaching is promising. Given the present findings, a practical, cost-effective bleaching sequence can probably be developed that employs only oxygen and peroxymonosulfate as oxidizing agents.

STRENGTHENING OF MECHANICAL PULPS AND RECYCLED FIBERS

Many studies have examined the use of oxidizing agents to enhance the strength properties of groundwood and thermomechanical pulps (16–18). Peroxymonosulfate might also be used for this purpose, and it might strengthen chemithermomechanical pulps as well. In addition, peroxymonosulfate might increase the strength properties of all types of recycled fibers (such as old newspapers and old corrugated containers). One particularly attractive possibility might be the delignification of old corrugated container fiber to produce a bleachable-grade pulp. Both the linerboard and corrugating medium portions of old corrugated containers contain about 10 to 15 percent lignin. Peroxymonosulfate treatment, followed by alkaline extraction, might be used to reduce the lignin content to a bleachable level (<5 percent) and the pulp then bleached. Such a bleached pulp should be lower in cost than pulp from virgin fiber and should find many uses in printing and writing and other grades of paper.

CONCLUSIONS

Based on the studies conducted to date, peroxymonosulfate pulping of fiberized hardwoods and annual plants appears to be very close to economic viability. Somewhat cheaper methods for producing peroxymonosulfate would favorably affect the economics of peroxymonosulfate pulping and make it competitive with present chemical pulping processes. The peroxymonosulfate pulping method produces strong pulps. has lower capital requirements, and is less environmentally troublesome compared with current processes. However, pulping of softwoods with peroxymonosulfate is very unlikely to be economically feasible because of the great consumption of oxidant.

Unbleached kraft pulps were found to be readily delignified with acidic peroxymonosulfate. Delignified kraft pulps, containing about 1 percent lignin, were readily bleached with alkaline peroxymonosulfate. Based on these results, a practical bleaching sequence can probably be developed employing only peroxymonosulfate and oxygen as the oxidizing agents. No chlorine or chlorine-containing compounds would be required, thus avoiding all production of chloro-organic compounds and eliminating this source of environmental pollution. In the absence of chlorine compounds, the bleaching liquors could be fed directly into the pulp mill chemical recovery cycle. This potential bleaching sequence requires further study.

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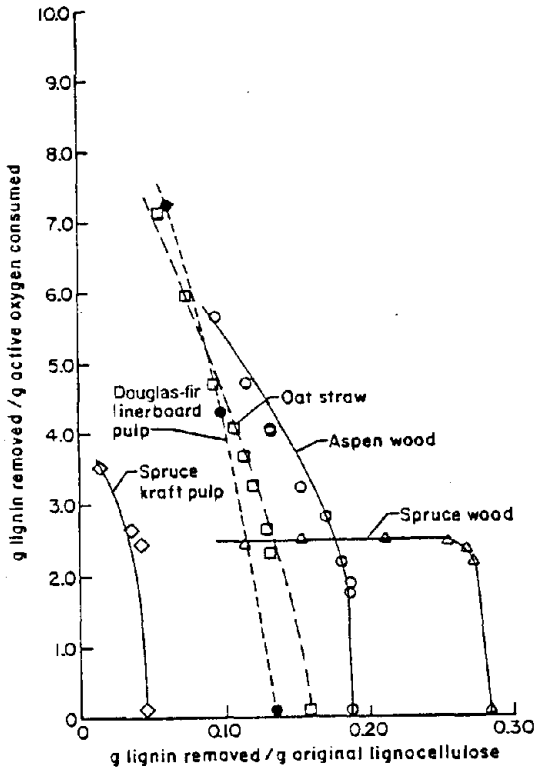

Figure 1: Oxidant consumption as a function of the amount of lignin removed for several lignocelluloses.

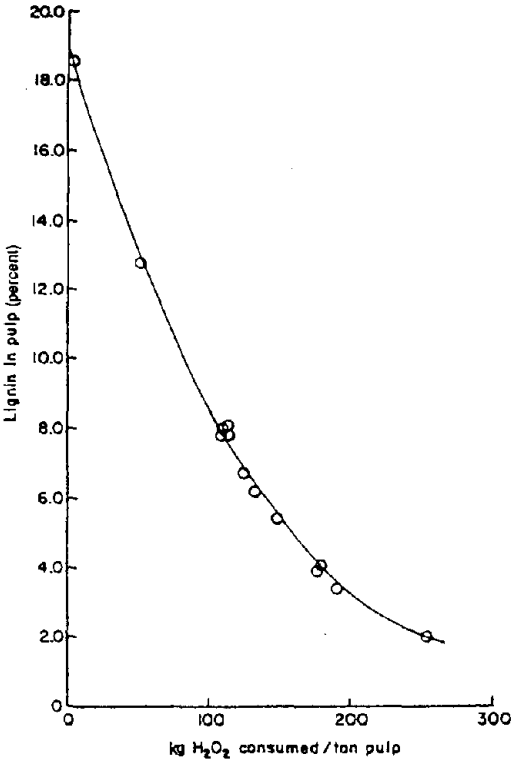

Figure 3: Residual lignin in pulp as function of oxidant consumption (H_2O_2) for range of reaction conditions.

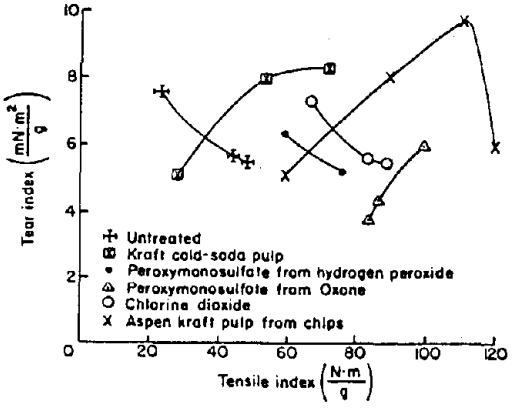

Figure 2: Handsheet (60 g/m^2) strength properties of treated aspen hardboard fiber (80 percent aspen. 20 percent mixed northern hardwoods).

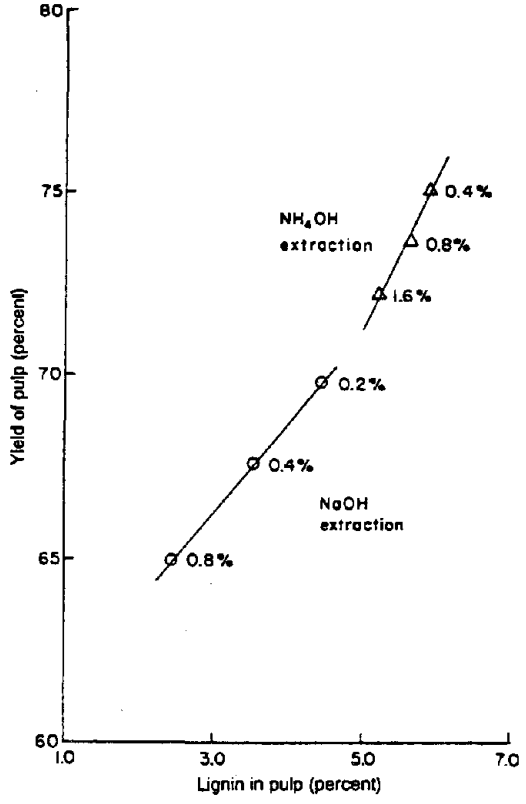

Figure 4: Comparison of ammonium hydroxide extraction and sodium hydroxide extraction of peroxymonosulfate-treated aspen hardboard fiber.

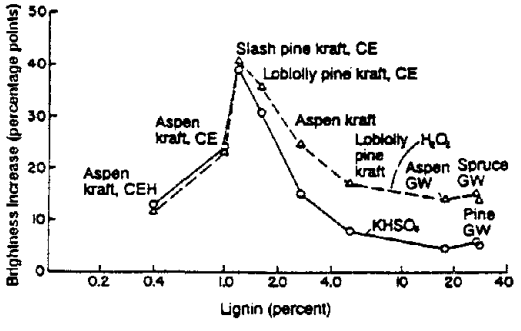

Figure 5: Brightness increase as a function of pulp lignin content in alkaline hydrogen peroxide and alkaline peroxymonosulfate bleaching of various pulps. CE is chlorination followed by alkaline extraction; CEH is chlorination followed by alkaline extraction and then hypochlorite treatment; GW is groundwood.

Table I. Delignification of 0.42-mm (40-mesh) aspen wood (1.00 g) using peroxymonosulfate at 22°C

HSO_5^- source	HSO_5^- in initial solution (percent)	HSO_5^- consumed (percent)	Liquor-to-wood ratio	Initial pH	Treatment time (days)	Residue yield (percent)	Lignin in residue[a] (percent)	TAPPI viscosity[b] (mPa·s)
H_2O_2 + H_2SO_4	4.9	42	25:1	0.2 (1.05 M)	1	60	0.4	11
Oxone[c]	4.9	38	25.1	1.6	1	63	2.8	27

[a] 19.9 percent lignin in original wood; values given are percentage of residue.
[b] TAPPI standard T230 om–82.
[c] 2 $KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$.

Table II. Peroxymonosulfate and chlorine dioxide pulping conditions

Pulping method	Time (h)	Temperature (°C)	Reagent	Weight of reagent applied (g)	Volume of 97 percent H_2SO_4 (ml)	Total water (ml)	Fiber weight[a] (dry basis) (g)	Yield (percent)	Kappa no.	Canadian standard freeness (unbeaten pulp) (ml)
Peroxymonosulfate	24	25[b]	H_2O_2	22.4[c]	40[d]	1,803	102	65.2	43	710
Peroxymonosulfate	2	50	Oxone	699.0	117	1,533	110	56.7	10.5	590
Chlorine dioxide	2	50	$C10_2$	5.8	0	1,648	110	65.2	39.8	740

[a] Fiber consisted of 80 percent aspen and 20 percent mixed northern hardwoods.
[b] Average room temperature.
[c] Total weight of initial H_2O_2 from a 70-percent solution, 74 percent conversion to H_2SO_5; 60 percent H_2SO_5 consumed in pulping.
[d] Calculated total acid remaining as H_2SO_4 after partial neutralization with 58 g KOH. 69 ml of 97 percent H_2SO_4 initially added.

Table III. Kraft pulping conditions for hardboard fiber and aspen chips[a]

Initial fiber type	Active alkali (percent)	Liquor-to-wood ratio	Time at 80°C–170°C (min)	Time at 170°C (min)	Yield (percent)	Kappa no.	Canadian standard freeness (unbeaten pulp) (ml)
Aspen chips	15.5	4:1	60	75	52.5	14.7	615

[a] Sulfidityof 25 percent for all fiber types.
[b] Mixture of 80 percent aspen and 20 percent mixed northern hardwoods.

Table IV. Hydrogen peroxide consumed in delignifying aspen hardboard fiber with peroxymonosulfuric acid

Sample	H_2SO_5 in initial solution (percent)	Liquor-to-wood ratio	Initial pH	Treatment time (days)	Yield (percent)	Lignin in pulp (percent)	H_2O_2 consumed (kg/ton pulp)
1	0.89	10:1	0.2	6	70	12.8	51
2	2.0	10:1	0.7	6	64	7.9	110
3	2.1	10:1	0.7	6	64	8.1	114
4	3.9	10:1	0.2	6	64	7.8	114
5	1.2	20:1	0.7	3	65	7.8	111
6	1.4	20:1	0.6	3	64	6.7	126
7	2.5	10:1	0.5	3	63	6.2	133
8	2.8	10:1	0.4	3	62	5.4	149
9	3.1	10:1	0.6	6	60	4.1	179
10	3.1	10:1	0.1	6	60	3.9	177
11	0.95[a]	10:1	0.2	6	58	3.4	191
12	4.1	10:1	0.5	6	57	2.0	253

[a] Only 8 percent conversion of H_2O_2 to H_2SO_2 (used 30 percent H_2O_2); 78 percent conversion in other samples.

Table V. Delignification of aspen hardboard fiber with peroxydisulfate at 22°C[a]

$S_2O_8^{=}$ source	$S_2O_8^{=}$ in initial solution (percent)	$CuSO_4$ in initial solution (percent)	Liquor-to-wood ratio	Initial pH	Treatment time (days)	Yield (percent)	Lignin in pulp[b] (percent)
Ammonium persulfate	5.2	0.30	10:1	1.1	3	83	19
				0.2[c]	3	71	13
				0.1[c]	12	64	8.4
Potassium persulfate	5.2	0	10:1	0.1[c]	12	62	6.5
Ammonium persulfate	6.7	0	10:1	-0.1[c]	31	59	5.4
				-0.3[c]	31	58	4.8

[a] 1.90 g of fiber.
[b] 19.9 percent lignin in original fiber; values are percentage of residue.
[c] Acidified with H_2SO_4.