

PROJECT ADMINISTRATION DATA SHEET

ORIGINAL REVISION NO. _____

Project No./(Center No.) E-19-645 (R6294-OAO) GTRC/~~GTR~~ DATE 4 / 10 / 87

Project Director: Dr. J. S. Hsieh School/~~Lab~~ ChE

Sponsor: E.I. DuPont De Nemours and Company; Deepwater, NJ

Agreement No.: Research Project Agreement dated 3/27/87

Award Period: From 3/27/87 To 3/26/89 (Performance) 4/15/89 Reports

Sponsor Amount:	<u>New With This Change</u>	<u>Total to Date</u>
Contract Value: \$ _____	\$ _____	\$ 160,081 (includes \$14,553 IPR Fee
Funded: \$ _____	\$ _____	\$ 160,081 (includes \$14,553 IPR Fee

Cost Sharing No./(Center No.) _____ Cost Sharing: \$ _____

Title: Mechanism of Peroxide Bleaching

ADMINISTRATIVE DATA

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Military Security Classification: _____ ONR Resident Rep. is ACO: _____ Yes No
 (or) Company/Industrial Proprietary: Non-Disclosure Defense Priority Rating: _____

RESTRICTIONS

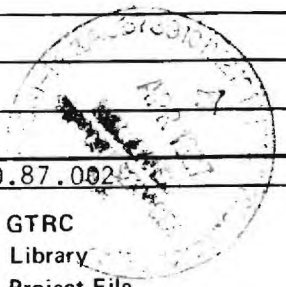
See Attached N/A Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval — Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of \$500 or 125% of approved proposal budget category.

Equipment: Title vests with N/A; none proposed

COMMENTS:

\$36,000 advance payment due from Sponsor within 30 days after receipt of fully executed agreement.



COPIES TO: _____ SPONSOR'S I.D. NO. 02.203.000.87.002

Project Director	Procurement/GTRI Supply Services	GTRC
Research Administrative Network	Research Security Services	Library
Research Property Management	Contract Support Div. (OCA)(2) <i>fa</i>	Project File
Accounting	Research Communications	Other _____

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Date 7/31/89

Project No. E-19-645

Center No. R6294-OA0

Project Director J. S. Hsieh

School/Lab ChE

Sponsor E. I. DuPont deNemours Co.

Contract/Grant No. Agreement dtd. 3/27/87

GTRC XX

GIT

Prime Contract No.

Title Mechanism of Peroxide Bleaching

Effective Completion Date 6/30/89

(Performance) 7/15/89

(Reports)

Closeout Actions Required:

 None

X Final Invoice or Copy of Last Invoice

X Final Report of Inventions and/or Subcontracts - Questionnaire sent to PI

 Government Property Inventory & Related Certificate

 Classified Material Certificate

 Release and Assignment

 Other

Includes Subproject No(s).

Subproject Under Main Project No.

Continues Project No.

Continued by Project No.

Distribution:

X Project Director

X Administrative Network

X Accounting

X Procurement/GTRI Supply Services

X Research Property Management

 Research Security Services

X Reports Coordinator (OCA)

X GTRC

X Project File

2 Contract Support Division (OCA)

 Other

ANNUAL REPORT

Primary focus of this project is the development of low-no chlorine based bleaching/delignification of chemical pulps with emphasis on increased use of hydrogen peroxide following the initial stage of a bleaching sequence.

Chlorine is generally used in the first stage of a conventional bleaching sequence. Due to environmental problems associated with the use of chlorine e.g. emission of chloroform, the use of oxygen in the first stage in the bleaching sequence has increased considerably in the past decade. However, in oxygen bleaching, as the delignification increases, the viscosity of the pulp decreases significantly below a particular kappa number. The viscosity (TAPPI STANDARD) is a measure of the degree of depolymerization or degradation of the cellulose. Pretreating the brownstock pulp prior to oxygen delignification can assist in the protection of the cellulose from the free radicals generated during the bleaching process.

Preliminary pretreatment experiments that were proposed to the Sponsor and conducted at Georgia Institute of Technology, showed promising results. A more thorough investigation was conducted in the Pulp and Paper Laboratory at Georgia Tech in the past year. A mechanism for the delignification has been developed based on experimental data and application of fundamental chemistry principles. Preliminary experiments have been conducted to simulate industrial conditions in the laboratory.

In the following year, plans are underway to develop strategies for the application of this technology in the paper mill. In addition, attempts will be made to develop novel bleaching sequences with increased use of hydrogen peroxide with process economics.

E-19-645

" MECHANISM OF PEROXIDE BLEACHING " PROJECT E-19-645

FINAL REPORT

SPONSOR: E. I. DU PONT DE NEMOURS & COMPANY
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DURATION OF THE PROJECT: 3/27/87 to 6/30/89

Submitted by:

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School of Chemical Engineering
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PRINCIPAL INVESTIGATOR:

DR. JEFFERY S. HSIEH

LIQUID-PHASE NITROSATION PRETREATMENT FOR OXYGEN DELIGNIFICATION OF KRAFT PULPS

ABSTRACT

Collaborative research on extended delignification of kraft pulps has shown that pretreatment with nitrosylsulfuric acid (NSA), a liquid nitrosating agent, under acidic conditions and in the presence of oxygen gives significantly improved delignification (kappa reduction) with good viscosity protection in the subsequent alkaline oxygen stage. Initial tensile, tear, burst and fold tests on the NSA-pretreated-OCED-bleached pulp, show values comparable to untreated-OCED pulp and suggest a potential for reduced chlorine and chlorine dioxide use.

The improved selectivity of delignification appears to result from the combination of the liquid reactant, oxygen and high-shear mixing. This efficiently forms 'activated' nitro-lignins which are more readily oxidized and hydrolyzed in the subsequent alkaline oxygen stage. Such a liquid-phase, high-shear 'prenitrosation' reaction offers a potentially competitive method to achieve extended delignification of kraft pulps in conjunction with the alkaline oxygen stage. This work, coupled with published work on nitrogen oxides pretreatment will lead to a better understanding of the mechanism of prenitrosation-prenitration reactions of lignin and promises to open ways to a more selective delignification of kraft pulps.

KEYWORDS

Pretreatment, softwood kraft pulp, oxygen delignification, high-shear mixer, nitrosylsulfuric acid, nitrosonium ion, nitrosation, nitration, selectivity, viscosity, kappa number, beatability.

INTRODUCTION

The use of chlorine to delignify kraft pulp is becoming increasingly undesirable because of the formation of environmentally unacceptable chloro-organics in the process and their presence in the aqueous effluents and air emissions. Once formed, the chloro-organics can not be readily and economically abated,

and therefore, technologies have been and are being developed to reduce the use of chlorine in particular and active chlorine compounds in general in bleaching of kraft pulps. The so-called extended delignification processes (1, 2, 3) include improvements in pulping as well as bleaching technologies to reduce the chlorinated organic formation without sacrificing the bleached pulp properties.

One of the more recent and widely commercialized technologies (4) is the alkaline oxygen delignification of kraft brown stock, before the conventional chlorine stage. The oxygen stage reduces the kappa number by about 50%, enabling significant reduction in chlorine use and corresponding reduction in chloro-organics in the plant discharges.

One of the limitations of oxygen bleaching is that beyond about 50% delignification (i.e., kappa reduction), the viscosity losses become severe and unacceptable. This loss of selectivity has kept oxygen delignification from advancing further to displace even more chlorine. However, more recent developments in the area of pretreatment of brown stock with nitrogen oxides before conventional oxygen delignification has opened up the possibility of achieving increased delignification with satisfactory viscosity protection.

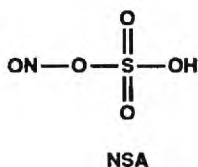
There is considerable literature involving the use of nitrogen oxides in delignification of chemical pulps. Clarke (5) studied the use of nitrogen dioxide as a substitute for chlorine in the bleaching of cellulose pulp; however, considerable cellulose degradation was observed, thereby limiting the use of nitrogen dioxide in the first bleaching stage. Brink (6) described the use of nitric oxide pretreatment followed by reaction with oxygen, to generate nitric acid *in situ*, and finishing with an alkaline extraction stage to delignify the pulp. In a series of articles and patents, Samuelson and coworkers (7-14) defined the chemistry and the practicality of pretreatment with nitrogen dioxide, under a variety of conditions and in the presence of nitric oxide, nitric acid and nitrate. This work culminated in the installation of a pilot plant in Sweden (15) directed toward a commercial demonstration of the process. Süss and Krüger (16) described bleaching of sulfite pulps with nitrogen dioxide, oxygen and hydrogen peroxide and observed that nitrous acid produced *in situ* plays a dominant role in NO_2 bleaching, and confirmed that it is an active delignifying agent. Recently Samuelson (17) reported that pretreatment with active nitrogen compounds permits the production of fully bleached kraft pulp without the application of elementary chlorine.

Mechanistic studies by Lindeberg and Walding (18) and Gellerstedt and Robert (19) have helped to shed light on the lignin 'activation' that occurs on pretreatment with nitrogen dioxide, and which results in a more selective alkaline oxidative delignification of kraft pulps.

In order to understand the nitrogen oxide pretreatment chemistry better we initiated work to use liquid-phase nitrosating agents as the pretreatment chemicals. It was not clear if there would be any favorable reaction or activity of the nitrosating agents toward lignin. The liquid nitrosating agents are the carriers of nitrosonium (NO^+) or nitroacidium (H_2NO_2^+) ions, which are known to nitrosate phenolics or aryl ethers (20, 21) in o- and/or p-positions. However, it was not known if these acidic

reagents would preferentially 'activate' the lignin on one hand or oxidatively and hydrolytically attack the cellulose fraction in the pulp on the other. Because the nitrosonium ion is more electrophilic than NO₂ gas (21, 22), it was expected to be faster-reacting than NO₂ with the electron rich centers in the pulp.

This report represents our preliminary work on pretreatment of softwood kraft pulps with nitrosylsulfuric acid (NSA) before alkaline oxygen delignification.



There are numerous nitrosating agents available (23), including nitrosyl halides, nitrosyltetrafluoroborates, nitrosyl acetate, nitrous acid, etc. However, because of its relative stability, commercial availability and ease and safety of use, NSA was used as the nitrosating reagent of choice for this initial investigation.

MATERIAL AND METHODS

Pulp

Southern pine kraft brown stock was used in this investigation. All chemical percentages added are on oven dry (O.D.) pulp basis.

Nitrosylsulfuric acid (CAS Registry No. 7782-78-7)

NSA was used as a 40% solution in 87% sulfuric acid corresponding to the product composition of 40% NSA, 52.2% H₂SO₄ and 7.8% H₂O, as available commercially from the Du Pont Company, Wilmington, Delaware. The chemical reacts with water to give nitric acid, sulfuric acid and oxides of nitrogen. Therefore, precautions were taken to dry the addition equipment and tubing thoroughly to avoid NSA decomposition before its contact with the pulp under high-shear conditions. Oxygen gas was used to force NSA into the fluidized pulp in the reactor.

Reactor

The schematic of the laboratory reactor, which was equipped with high-shear mixer, is given as Figure 1.

The cylindrical reactor (I.D. 10.2 cm), placed on the horizontal axis, had four mixing blades (impellers), each blade 14.0 cm × 2.1 cm × 0.6 cm. The diameter of the shaft plus the blades was about 7.6 cm. Three hollow baffles (14.0 cm × 0.6 cm × 0.6 cm each) were positioned at 120° to each other. The clearance between the blade tips and the baffles was 0.6 cm. Each baffle had 9 holes, ~0.04 cm diameter each, to inject the reagents and O₂ into the reactor. The reactor could be charged/discharged at

one end by removing a fluoropolymer gasketed circular stainless steel plate held by six nuts.

The impellers were powered by a 20 horsepower motor and could be run safely at up to 5,000 rpm. The tip speed (m/sec) of the impellers was calculated as 0.8 at 200 rpm, 4.0 at 1,000 rpm and 12.0 at 3,000 rpm. The normal procedure for the reactor operation was to fluidize the pulp at 10% consistency by mixing at 300 rpm. The reagents were then forced into the reactor by means of O₂ through the check valve(s) and the perforated baffles while mixing at 1,000-3,000 rpm. After an initial mixing time at the higher rpm, the pulp was further mixed at 200 rpm to complete the reaction.

The reactor was electrically heated and could be pressurized. Both acidic NSA/O₂ pretreatment and alkaline O₂ delignification were done in the same reactor.

NSA Pretreatment

NSA was introduced into the preheated reactor under oxygen pressure at 276 kPa (40 psig) via the check valve into the perforated baffle. The amount on 100% active ingredient basis was 0.5 to 2% (1.25 to 5.0% commodity basis).

The mixing, under 276 kPa O₂, was done at 1,000-3,000 rpm for 5 sec to 15 min at 25°C to 48°C. After an optional ~15 min period of mixing at ~200 rpm, the pulp was discharged from the reactor and washed twice with tap water to remove the free acidity. This pulp was then subjected to O₂ delignification.

The NSA pretreatment stage has been designated as the n stage in this study.

Oxygen Delignification

The pretreated, washed pulp was charged at 10% consistency to the reactor, heated to 100°C and mixed at 300 rpm. MgSO₄ (0.04 to 0.2wt% Mg⁺⁺ on O.D. basis pulp) was introduced into the

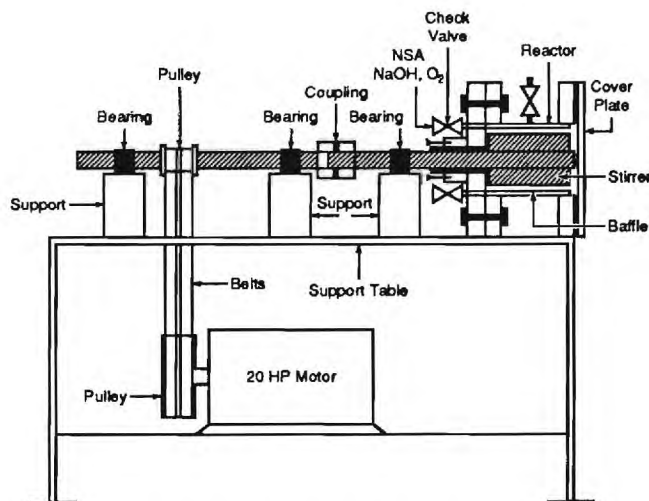


Figure 1: Schematic of high-shear mixer for NSA-pretreatment and oxygen bleaching.

reactor. After one minute, 4-8% NaOH was introduced with 689 kPa (100 psig) O₂. After 30 min mixing at 100°C, the pulp was discharged, washed twice with tap water and air-dried. The kappa number and viscosity of the pulp were then determined.

Test Procedures

Handsheets were prepared according to TAPPI T 205 om-80, and were tested for GE brightness, tensile index, tensile energy absorption, folding endurance, tear index and burst index, according to TAPPI T 220 om-83, and the specific references therein.

Kappa number and CED viscosity were determined according to standard TAPPI methods, T 236 hm-85 and T 230 om-82 respectively.

The loss of brightness due to heat was measured after exposing the handsheets to 105°C for 24 hours in an electrical oven.

Pulp beating was done in a PFI beater, and the Canadian Standard Freeness was determined according to CPPA Standard C.1.

Selectivity

Selectivity of delignification is expressed as the fraction,

$$\frac{(\text{final viscosity} - \text{initial viscosity})}{(\text{final kappa no.} - \text{initial kappa no.})}$$

RESULTS AND DISCUSSION

NSA Pretreatment Parameters

In the initial scouting experiments it was determined that the pretreatment temperature, concentration and the mixing efficiency, at a given consistency, were critical to the efficient delignification of the pulp without unacceptable viscosity loss. Therefore, optimum pretreatment temperature, concentration and mixing conditions were defined. Figures 2, 3 and 4 show the results. The goal was to obtain the highest selectivity as compared to oxygen delignification. As noted earlier, all the experiments were run at 10% consistency and no attempts were made to optimize the pretreatment based on higher consistency reaction.

Pretreatment Temperature

The optimum pretreatment temperature for 1% NSA use (Figure 2) was determined to be about 40°C. At higher temperatures, there was noticeable loss of selectivity. At 25°C, while the selectivity was good, kappa reduction was inferior, most likely for kinetic reasons. However, the lower temperature would be preferred for protecting the pulp from acid hydrolysis. Therefore, further optimization may be necessary.

NSA Concentration on Pulp

The amount of NSA was varied between 0.5% and 2% on O.D. pulp. Figure 3 shows the effect of concentration of NSA on

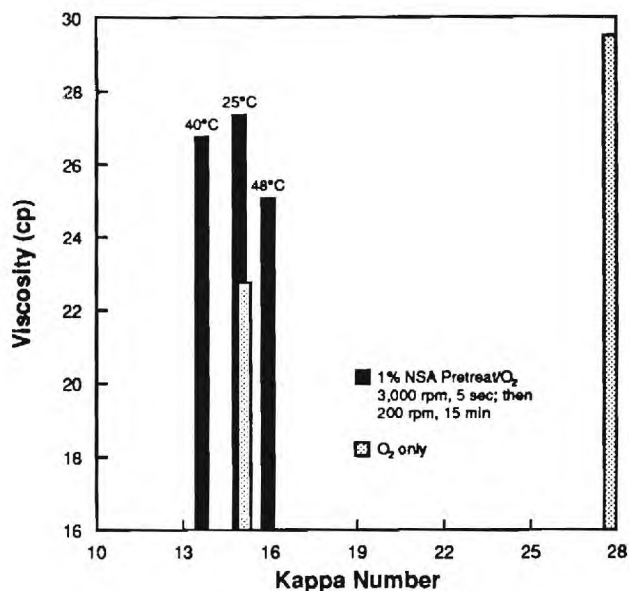


Figure 2: Effect of pretreatment temperature.

kappa no. and viscosity. Data for these experiments are given in Table 1.

As can be seen, the 1 and 2% NSA pretreatments gave high selectivity of delignification (0.26 and 0.21 respectively). The ineffectiveness of 0.5% NSA pretreatment was most likely due to both the low active reagent concentration and the lack of acidity in the reaction. The amount of sulfuric acid value in 0.5% NSA was too small to acidify the slightly alkaline brown stock to the desired pH (about 2). It is known (24) that with decreasing acidity the NO⁺ ion in NSA converts first to nitroacidium ion (H₂NO₂⁺) and finally to HNO₂. Since NO⁺ species predominates

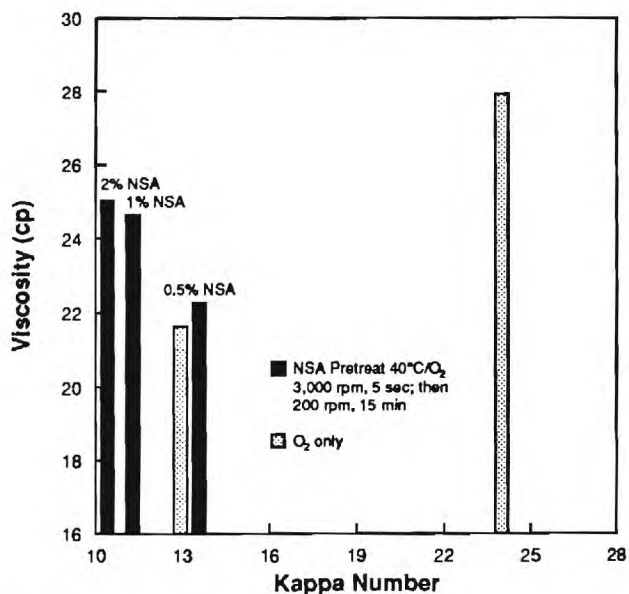


Figure 3: Effect of NSA concentration.

Table 1: Effect of NSA concentration on kappa number and viscosity.

PULP - Southern pine kraft brown stock
 EXPERIMENT 1 - O₂ Stage: T = 100°C, P = 689 kPa oxygen pressure, consistency = 10%, t = 30 min, 200 rpm, NaOH conc. = 5.5%, Mg⁺⁺ (MgSO₄) = 0.16%.
 EXPERIMENT 2* - 0.5% NSA + Wash + Expt. 1
 EXPERIMENT 3* - 1% NSA + Wash + Expt. 1
 EXPERIMENT 4* - 2% NSA + Wash + Expt. 1

*Pretreatment was done at 40°C with 276 kPa O₂ pressure and mixed at 1000 rpm for 1 minute followed by 200 rpm for 14 minutes.

Expt. #	Kappa #	Viscosity (cp)	pH at End of		Percent Reduction		Selectivity
			Pretreatment	O ₂ Stage	Kappa #	Visc. (cp)	
Brown stock	24.0	27.8	—	—			
1	12.9	21.5	—	—	46.3	22.7	0.57
2	13.5	22.1	5.7	11.8	43.8	20.5	0.54
3	11.3	24.5	2.1	12.0	52.9	11.9	0.26
4	10.4	24.9	1.9	11.7	56.7	10.4	0.21

under strongly acid conditions, and if it is indeed the effective lignin 'activating' entity, then the poor performance of 0.5% NSA is understandable.

Effect of Mixing

Efficient mixing during pretreatment was found to be the most important factor in achieving high selectivity of delignification in the alkaline oxygen stage. The key was to mix the strongly acidic and reactive NSA under such high-intensity conditions that intimate, uniform and rapid contact would be achieved between NSA and the pulp fibers. As Figure 4 shows, highest selectivity was obtained in the alkaline oxygen stage when the NSA pretreatment was done at 1,000-3,000 rpm (4-12 m/sec tip speed). Optimum mixing apparently took place in a few to several seconds, suggesting that longer time at high intensity may not be necessary. At 200 rpm (0.8 m/sec tip speed) the selectivity dropped substantially.

With optimum mixing of the nitrosating agent coupled with a higher consistency reaction, the pretreatment efficiency and selectivity could be much higher, leading to potentially significant reduction in the amounts of the pretreatment chemical used.

Selectivity of Delignification

Figure 5 shows the direct comparison between an NSA-pretreated kraft brown stock and the O₂ control. The data for these experiments are given in Table 2. Progressive reduction in kappa number was achieved by increasing the amount of caustic

with the rest of the conditions held constant. It can be seen that the NSA pretreatment has significantly improved the selectivity of delignification. Thus at a kappa no. of 14 or 50% reduction from the original kappa value, the O₂ bleached pulp loses 32% of its viscosity. However, at the same kappa no., the NSA-pretreated pulp shows only about 7.8% viscosity loss, an improvement of about 40.6% in viscosity. At 50% kappa no.

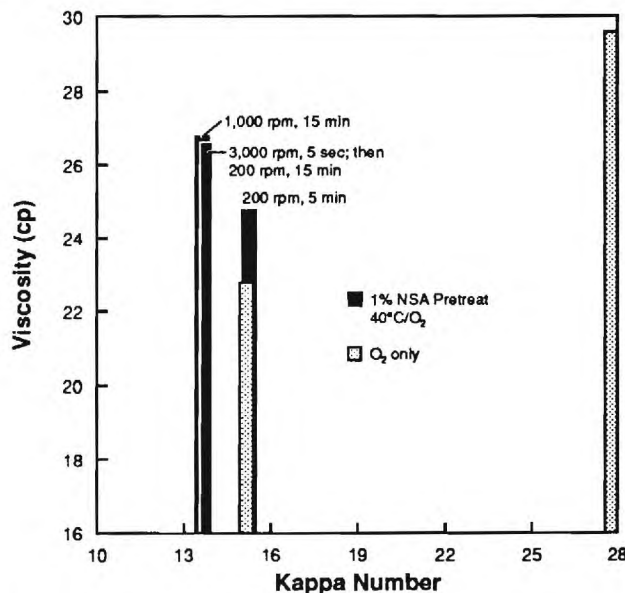


Figure 4: Effect of mixing.

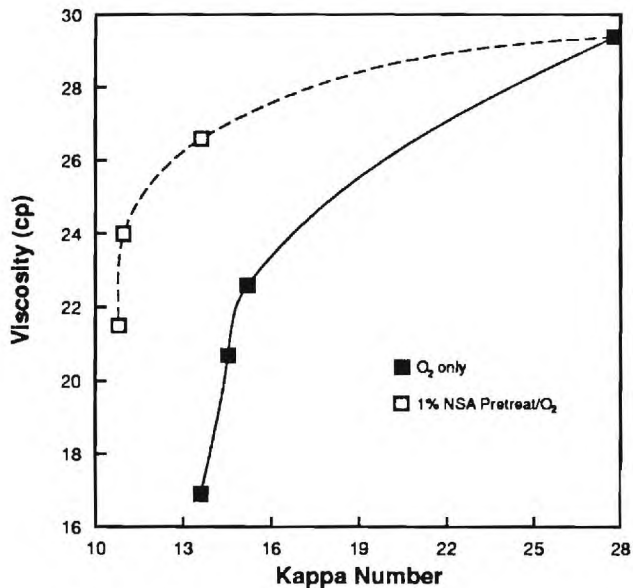


Figure 5: Viscosity vs. kappa number.

reduction, the selectivity for O₂ control is 0.67 while that for the NSA-pretreated O₂ bleach is 0.16. Furthermore, at the same viscosity of 21.5 cp, the NSA-pretreated pulp shows a kappa no. of 10.8 while the O₂ control pulp shows a kappa no. of about 14.8. This represents a kappa improvement of 27% at the same viscosity due to the NSA pretreatment. As the lignin concentration decreases, the oxidative and hydrolytic attack by alkaline

O₂ on non-lignin fraction of the pulp would increase. Therefore the relative preservation of selectivity at low kappa values by NSA pretreatment suggests that this pretreatment protects the cellulose from the damaging attack by oxygen-based free radicals formed in the alkaline oxygen stage.

It is expected that with further optimization of the nitrosation pretreatment selectivity of delignification of kraft pulps can be improved further.

To determine if this selectivity advantage will persist across a standard full bleach sequence, southern pine brown stock of 28.3 kappa no. and 23.2 (cp) viscosity was fully bleached in an OCEDED sequence, with and without NSA pretreatment. Figure 6 and Table 3 show the results. In order to properly control the viscosity drop, a kappa factor of .164 was used. About 2.7% chlorine and 1.2% ClO₂ were used in C and D1 stages respectively. These concentrations are ~40-50% lower than the quantities normally used in a standard CEDED bleaching to high brightnesses. The final brightnesses were a modest 78.3 (O₂ only) and 78.4 (NSA/O₂). As Figure 6 shows the NSA pretreatment protected the pulp viscosity throughout the sequence. There was a 19% viscosity improvement in nOCEDED over OCEDED pulp. This further suggests that much of the viscosity protection given to the pulp by NSA pretreatment is not negated by the downstream oxidative bleaching stages.

Because of the high selectivity and reactivity at moderate temperatures, and ease of handling, liquid nitrosating agents, such as NSA, offer an alternate and potentially a low-investment pretreatment route to the extended delignification of kraft pulps.

Table 2: Variation of viscosity with kappa number.

NaOH Conc.	Kappa #	% Red	Viscosity (cp)	% Red	pH at End of		Selectivity
					Prestage	Oxygen	
Brown stock	27.9	—	29.4	—	—	—	—
Oxygen Delignification							
4%	15.2	45.5	22.6	23.1	—	11.8	.53
6%	14.5	48.0	20.7	29.6	—	12.2	.65
8%	13.5	51.6	16.9	42.5	—	12.5	.87
NSA Pretreatment/Oxygen Delignification							
4%	13.7	50.9	26.6	9.5	2.1	10.5	.20
6%	11.0	60.6	24.0	18.4	2.1	12.0	.32
8%	10.8	61.3	21.5	26.9	2.1	12.3	.46

Pretreatment: 1% NSA, 40°C, 276 kPa O₂, 3,000 rpm for 5 sec then 200 rpm for 15 minutes.

Oxygen Stage: 689 kPa O₂, 100°C, 200 rpm mixing, 30 min, Mg⁺⁺ = 0.16% (as MgSO₄), NaOH concentration 4, 6, 8%; 10% cons.

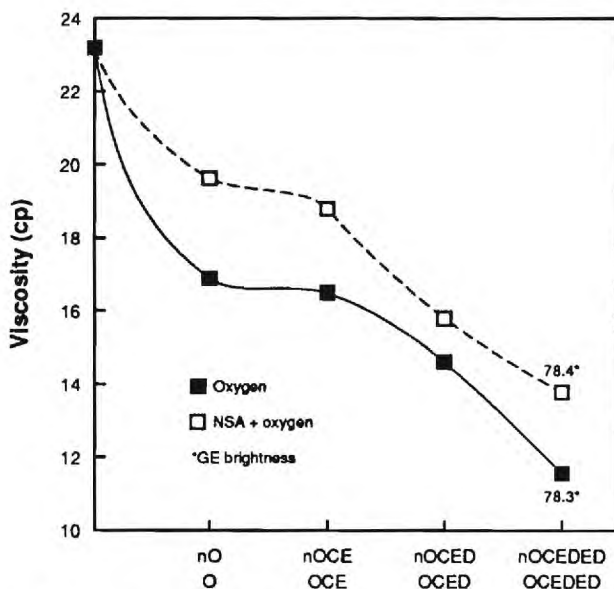


Figure 6: Viscosity profile of nOCEDED vs. OCEDED pulps.

Beating Study and Pulp Property Testing

Comparative tests were run on another sample of softwood kraft brown stock bleached with sequences nOCEDED, OCEDED and CEDED. The pulp was bleached according to the conditions in Table 4. These results represent our initial look into the mechanical properties of the pulp. No effort was made to optimize the C or D stages to obtain the best pulp performance. Because no consideration was given to the likely structural modification of the pulp due to NSA, the pulp was probably overchlorinated. Note that the nOCEDED pulp viscosity was lower than those of both OCEDED and CEDED pulps (Table 4). The three bleached pulps were beaten in a PFI mill at 0 to 7,000 revolutions and their properties tested at various freenesses.

Figures 7-12 show the results of these tests.

Figure 7 shows that both the OCEDED and nOCEDED pulps are easier to refine and are very similar in their beating characteristics. There is a close similarity between nOCEDED and OCEDED pulps.

Figure 8-12 represent tear, tensile, tensile energy absorption, burst, and folding endurance properties as a function of freeness. The OCEDED and nOCEDED pulps are very similar to each other above ~500-600 CSF values. At lower freenesses the nOCEDED pulp shows a trend toward lower strengths or higher tensile energy absorption. This suggests that the nOCEDED pulp has probably suffered incipient fiber weakening, which under conditions of greater refining (i.e., low CSF) results in fiber damage. This suggests the need to reduce chlorine further to improve the mechanical properties of the pretreated pulp.

Heat Stability of nOCEDED Pulp

The three pulps discussed in the preceding section were tested for their brightness stability at 105°C for 24 hours. Table 4 gives the details. Of particular significance is the reduced reversion by 9.0 brightness points in nOCEDED pulp against the OCEDED pulp at comparable viscosities. nOCEDED pulp also reverted 8.7 points less than the CEDED pulp, but the viscosity of the CEDED pulp was higher.

At this point it is not known if the n stage itself stabilized the heat-sensitive precursors in the nOCEDED pulp or the 'overchlorination' of the n pulp resulted in a more efficient removal of those precursors.

CONCLUSIONS

Pretreatment at low pH with nitrosating agents, which are the carriers of nitrosonium ion (NO^+), offers a potentially more selective way to delignify softwood kraft pulps in the alkaline oxygen stage, and thereby reduce or eliminate the use of chlorine and the formation of undesirable chloroorganics.

Nitrosylsulfuric acid, a nitrosating agent, was successfully used as a representative, convenient, relatively safe and easy to handle source of nitrosonium ions for pretreatment of softwood kraft pulps before oxygen delignification.

Nitrosylsulfuric acid was used with high-shear mixing to promote rapid, uniform and intimate contact and reaction with the pulp. Under such an optimal mixing, the equilibration of NO^+ ion to HNO_2 was minimized and the selectivity of delignification was increased. The increased selectivity of delignification results in substantial improvement in CED viscosity at a given kappa number, or a significant reduction of kappa number at a given viscosity. Also the NSA pretreatment significantly improved the heat stability of a fully bleached OCEDED pulp.

The beatability and mechanical properties of tear, tensile, tensile absorption, burst, and folding endurance of nOCEDED pulp were very similar to the OCEDED control. However there were indications that the pretreated pulp had suffered fiber weakening, most likely due to overchlorination. Further optimization in Cl_2 and ClO_2 use should improve these properties.

Because of the high selectivity and reactivity, and ease of handling, liquid nitrosating agents, such as NSA, offer an alternate and potentially a low-investment route to the extended delignification of kraft pulps.

Further work is needed to optimize the n stage and to define more precisely its positive impact on chlorine reduction or elimination, heat stability and mechanical properties of the bleached pulp.

Finally, the reaction of nitrosating agents with pulps should help develop a precise mechanism of lignin nitrosation-nitration.

Table 3: Viscosity profile of nOCEDED vs. OCEDED

	<u>Pulp</u>	<u>Kappa #</u>	<u>% Red</u>	<u>Viscosity (cp)</u>	<u>% Red*</u>	<u>Brightness</u>
	Brown stock	28.3	—	23.2	—	—
O ₂	1**	16.9	40.3	16.9	27.2	—
	2***	16.2	42.8	19.6	15.5	—
CE	1	7.8	72.4	16.5	28.9	—
	2	7.5	73.5	18.8	19.0	—
CED	1	—	—	14.6	37.1	—
	2	—	—	15.8	31.9	—
CEDED	1	—	—	11.6	50.0	78.3
	2	—	—	13.8	40.5	78.4

*Percentage reduction is based on brown stock kappa number and viscosity

**Pulp 1: Oxygen delignified pulp

***Pulp 2: NSA pretreatment followed by oxygen delignification

Pulp: Southern pine brown stock.

NSA Pretreatment: 10% cons.; 1% NSA; 40°C; 276 kPa O₂; mixing at 3,000 rpm for 5 sec, then 200 rpm for 15 min. Pulp washed twice with tap water before O Stage.

O Stage: 10% cons.; 689 kPa O₂; 200 rpm mixing; 30 min; 4% NaOH; 0.2% Mg⁺⁺ (as MgSO₄). Pulp was washed and air-dried.

C Stage: 2.77% and 2.66% Cl₂ for O and nO pulps respectively, 30°C, 30 min, 3.5% cons.

E₁ Stage: 5% NaOH at 70°C for 90 min at 10% cons.

D₁ Stage: 1.2% at 70°C for 180 min at 10% cons.

E₂ Stage: 3.5% NaOH at 70°C for 90 min at 10% cons.

D₂ Stage: 2.0% ClO₂ at 70°C for 180 min at 10% cons.

Table 4: Comparative bleaching and heat stability of softwood kraft pulp.

	<u>CEDED</u>	<u>OCEDED</u>	<u>nOCEDED</u>
Kappa # (Before C Stage)	30.1	16.1	14.7
Chlorine Charge (%)	6.622	3.542	3.234
Initial Brightness (GE)	87.55	89.57	89.37
Final Brightness (105°C/24 Hrs)	67.19	68.87	77.70
Brightness Difference	20.36	20.70	11.67
% Reversion	23.3	23.1	13.1
CED Viscosity	9.56	7.39	6.75

N Stage: 1% Charge; 5 sec at 3,000 rpm, 15 min at 200 rpm; 40°C; 10% cons.

O Stage: 10% cons.; 689 kPa O₂; 200 rpm mixing; 30 min; 4% NaOH; 0.2% Mg⁺⁺ (as MgSO₄). Pulp was washed and air-dried.

C Stage: Chlorine charge: 0.22 × Kappa Number at 30°C for 30 min at 3.5% cons.

E₁ Stage: 5% NaOH at 60°C for 90 min at 10% cons.

D₁ Stage: 3% at 60°C for 180 min at 10% cons.

E₂ Stage: 4% NaOH at 60°C for 90 min at 10% cons.

D₂ Stage: 2% ClO₂ at 60°C for 180 min at 10% cons.

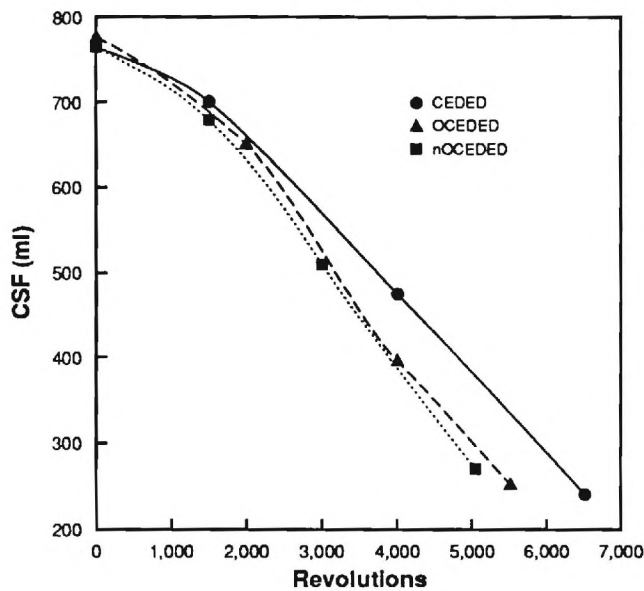


Figure 7: Canadian standard freeness vs. PFI mill revolutions.

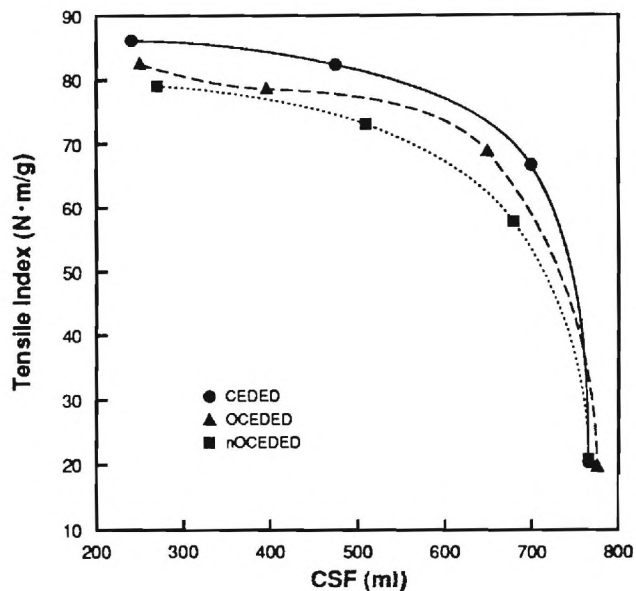


Figure 9: Tensile as a function of beating.

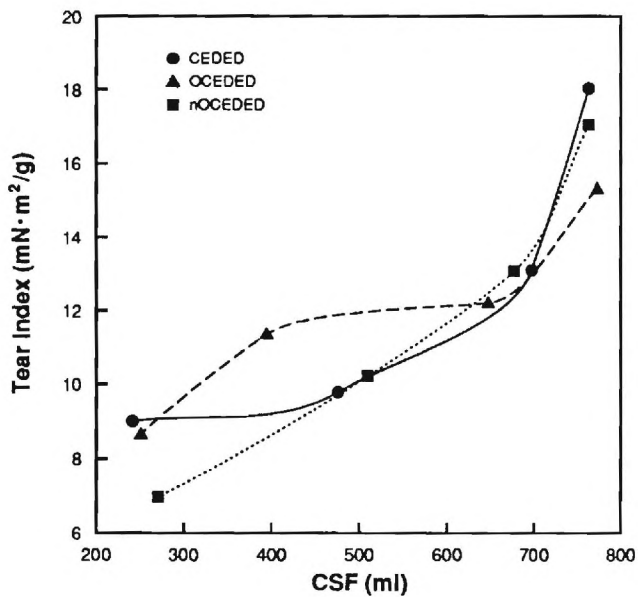


Figure 8: Tear index as a function of beating.

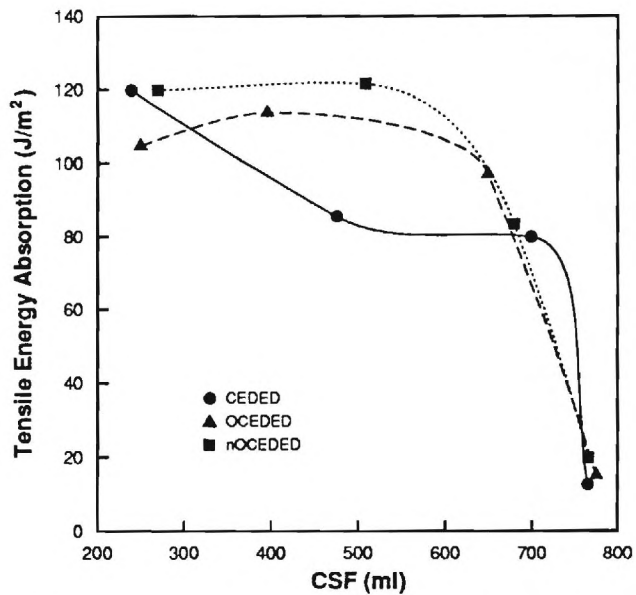


Figure 10: Tensile energy absorption as a function of beating.

This should have useful implications on strategies to reduce or eliminate the formation of chloro-organics in bleach plant effluent and emission streams.

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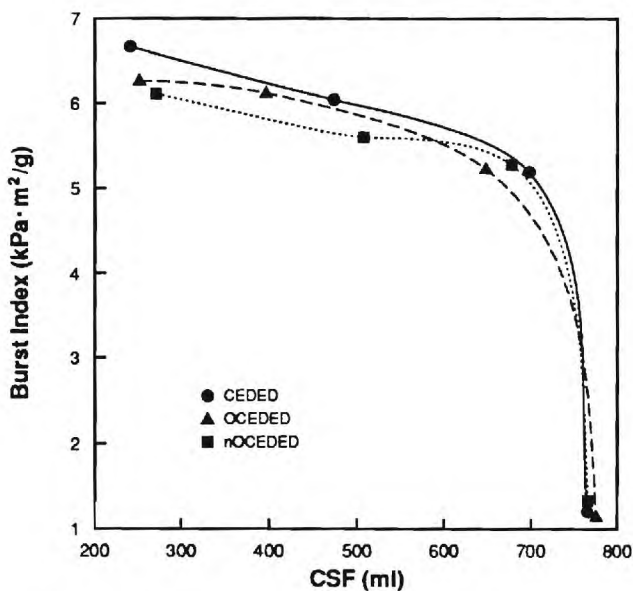


Figure 11: Burst index as a function of beating.

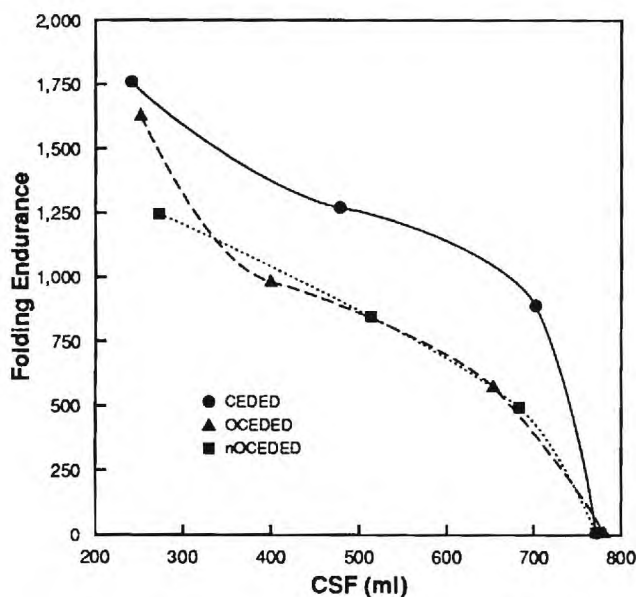


Figure 12: Folding endurance as a function of beating.

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