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THE EFFECTS OF ANTHRAQUINONE ON KRAFT PULPING

by

Allison K. Noble

A Thesis submitted to the Faculty of the Department of Paper Science & Engineering in partial fulfillment of the Degree of Bachelor of Science.

> Western Michigan University Kalamazoo, Michigan April 1978

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ABSTRACT

Popel chips were cooked in Kraft liquor modified by anthraquinone (AQ). Ten trials with varying levels of AQ, white liquor and cooking time were completed. It was found that the per cent yield decreased by as much as 10 points as the level of AQ was increased. But the Kappa number decreased by only 2 points at the maximum AQ level; therefore, at a constant Kappa number, the per cent yield for the unmodified Kraft pulp would be greater than the modified pulp. Overall pulp strength increased significantly with the addition of 0.05% AQ, as was evidenced by the improvement of strength for the zero revolution refined sample.

INTRODUCTION

During the 1960's, people everywhere became aware of the incredible degree to which their environment was being polluted. They learned that one of the major causes of pollution was the production of Kraft pulp. The resultant demand for zero pollution forced the pulp industry to search for a replacement for the Kraft process. Before this can be accomplished, one must fully understand the advantages and disadvantages of the Kraft process and what must be done to improve it.

THE KRAFT PROCESS

The Kraft process has been virtually unchanged for the past fifty years. The process utilizes white liquor, which is composed of sodium hydroxide and sodium sulfide. The liquor is added to wood chips in a digester, heated to a maxiumum temperature for a specified length of time, then removed, washed and refined. The pulp is then sent to either the bleach plant or the paper machine. This is a versatile process that is capable of producing a pulp of excellent strength and quality from a variety of wood species. The process also maintains a high chemical and energy efficiency. But major disadvantages are also associated with the Kraft process. These include:

- 1. Inferior yields
- 2. High capital expenditures
- 3. Severe air and water pollution
- Nonselectivity of lignin removal results in high carbohydrate losses.¹

This loss of carbohydrates is damaging because it results in a severe reduction of the per cent yield, and if excessive, can affect the sheet strength. It has been determined that 20% of all polysaccharides are lost in the Kraft process, with losses especially high during the initial portion of the cook. This loss of carbohydrates is due to a degradation reaction, called the peeling reaction. The peeling reaction is basically a step-

- 2 -

wise reduction of the polysaccharide terminal aldose units. This process is continued until a stopping reaction occurs, which stabilizes the polysaccharide against further attack.²

Several attempts have been made to find a method of slowing or preventing the peeling reaction. These include the use of polysulfide, sodium borohydride and hydrazine, but as yet, these methods are too expensive to be used on a production level.³

Before any new process can be considered an alternative to the Kraft process, it must:

- Produce pulp of equal or better strength and per cent yield of Kraft.
- 2. Reduce the amount of energy required.
- 3. Allow for the recovery of by-products.
- 4. Have the ability to pulp most wood species.
- 5. Be free of inorganic sulfides that are capable of forming reduced (odoriferous) sulfur compounds.
- Avoid the use of strong acids or alkali in order to prevent the degradation of the cellulose and hemicellulose.
- Be capable of solubilizing the lignin without attacking the cellulose and hemicellulose, or modifying the lignin so that it can contribute to the desired end products.
- 8. Employ a simpler recovery process than that of Kraft and maintain a minimum pollution level.
- Have sound investment costs, in that it does not use multiple stages or significantly higher pressures, 4 temperatures or times than are currently being used.

Even when a proposed alternative fits all the above requirements, it must still pass one final test; the pulp's performance on the paper machine. Eventually, the paper machine may be forced to modify its basic design in order to keep up with the changes in pulp production.

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ALTERNATIVES TO THE KRAFT PROCESS

- 4 -

Within the last few years, the major pulp producers throughout the world have concentrated their research efforts in the direction of developing an acceptable alternative to the Kraft process. From this intensified research evolved several possible methods. These methods include:

- 1. Oxygen pulping
- 2. Nitrogen pulping
- 3. Amine pulping
- 4. Polysulfide pulping
- 5. Irradiation
- 6. Sulfite sulfide pulping
- 7. Holopulping
- 8. Chemical solvent pulping

Each new process will be briefly discussed.

Oxygen Pulping

Oxygen pulping, also called soda-oxygen delignification, was first introduced approximately ten years ago. At that time it was thought to be the cure-all for problems associated with the Kraft process. The major advantage of oxygen pulping is its low pollution level. The initial oxygen pulping process consists of a one-stage cook, which utilizes a low temperature in order to provide protection for the carbohydrates. But a long retention time at the maxiumum temperature is required in order to produce a uniform pulp.⁵ Other drawbacks of the oxygen pulping process include:

- 1. High corrosion, which requires the installation of special, expensive equipment.
- 2. Alkali must be added to maintain pH.
- 3. Increased degree to which the screens are plugged.
- 4. The reaction is exothermic; therefore, the digester must be cooled.
- 5. Uniform liquor flow must be maintained at all times.
- 6. High circulation rate must be maintained.
- 7. Long retention time required.
- 8. High energy cost.⁶

Pulp yield is equivalent to that of Kraft, 52-55%, but the quality and strength of the pulp is lower than Kraft.

In order to overcome some of the above disadvantages, researchers developed several modifications of the basic oxygen pulping method. Most of these variations have gone from a onestage process to a two-stage system.

One such system utilizes a semi-chemical first stage followed by a defiberization stage. The pulp is then sent to a vessel where it is reacted with oxygen and alkali. This process can be used for the delignification of very high yield pulps. Multiple oxygen stages with a very low alkali charge is also recommended, providing the added equipment expense is cost-effective. Pulp treated in this manner is easier to refine, yields a very dense sheet, has low tear strength, maintains a higher carbonyl content, and has an overall strength that is comparable to Kraft.⁷

Another variation of oxygen pulping is to treat wood chips with oxygen in the presence of either sodium hydroxide solution or a dilute sodium hydroxide-sodium sulfide solution. This mixture is then cooked with sodium cyanide. The resultant pulp

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has an exceptionally high yield.

A third oxygen pulping method is also a two-stage process, which utilizes only one cooking vessel. The first stage consists of downflow liquor circulation with upflow oxygen movement. The chips are not submerged. In the second stage, the chips are submerged in alkaline liquor. Oxygen-saturated liquor is then pumped radially through the chips and circulated throughout the vessel.⁸

The HOPES oxygen pulping process (high oxygen pulping enclosed system) is the newest and most practical approach to oxygen pulping. This process involves three steps:

- 1. Precook the chips in sodium carbonate solution in order to soften them.
- 2. Defibrate the chips mechanically.
- Cook the chips in a pressurized vessel with oxygencontaining gas.

This process can produce a wide variety of pulps, merely by controlling the degree of the oxidative reaction. This system can handle both hardwoods and softwoods. The pulp is brighter and easier to bleach than Kraft. The burst and tensile strengths are equal to that of Kraft, but the tear factor is less than that of Kraft. The major advantage of the HOPES process is that the waste liquor can be handled by current continuous liquor recovery systems. With only a slight investment, present Kraft mills can be converted to closed, pollution-free HOPES processes. The major disadvantage of this process is that some of the usual saleable by-products of the Kraft process are chemically reduced by the HOPES process and, therefore, cannot be sold.⁹

Nitrogen Pulping

Nitrogen pulping usually involves a two-stage process where the wood chips are exposed to either nitrogen dioxide in a solvent, such as carbon tetrachloride or nitric acid. Sodium nitrate may also be used during the first stage. The second stage is an extraction process, during which the chips are subjected to a 1-10% sodium hydroxide solution. Pulp produced from nitrogen pulping has a very high purity and, therefore, is well suited as a dissolving pulp. This pulp is easily bleached and produces a per cent yield of 60-83%. The delignification reaction occurs at a lower temperature than Kraft, but is more affected by chip moisture. Good strength properties are obtained from these pulps. The major advantage of nitrogen pulping is that stream pollution is virtually eliminated due to the fact that dilute pulp washings should prove beneficial as irrigation water.¹⁰ The major disadvantage of this process is that the pulp can be used only for specific pulping applications, ie., dissolving pulps.

Amine Pulping

There are two major compounds, when used in conjunction with typical soda liquor, have produced pulp of comparable quality to that of Kraft. They are:

1. Monoethanolamine (MEA)

2. Ethylenediamine (EDA)

These two compounds were added to normal soda cooks in small amounts. The rate of delignification and, therefore, the quality of the pulp produced is a function of the amine charge. At 10%

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EDA, the resulting pulp is better overall than soda, but not as good as Kraft. At 40% EDA, the pulp is approximately equal to Kraft. At levels of 60-80% EDA the pulp quality exceeds that of Kraft.¹¹

Pulp produced by the soda-amine process has a higher yield with a higher alpha-cellulose content than unmodified soda or Kraft pulps. For example, a soda-MEA cook has a per cent yield of 85-87%. A soda-EDA cook has a per cent yield of 87-89%. But a typical soda cook has a per cent yield of 82-83%, and a Kraft cook has a per cent yield of 84-85%.

Soda-amine pulps are easier to bleach than Kraft. They not only require less chlorine and chlorine dioxide, but also produce a brighter pulp.¹² The major disadvantage of soda-amine pulping is the excessive cost of MEA and EDA.

Polysulfide Pulping

Two different applications of the polysulfide process were developed. The first process consists of adding sulfur directly to the digester, or by oxidizing part of the sulfide in the Kraft white liquor to polysulfides. This results in an increased per cent yield of 4-7%. This method is inexpensive and the conversion of Kraft mills to this process is easily done. The major disadvantages of this process are that the sulfur increases the corrosion of the equipment, and the liquor needs to be handled carefully during its preparation.¹³

The second application is to pretreat the chips, in a special vessel, with hydrogen sulfide in the presence of alkali under heat and pressure. This is then followed by a normal Kraft cook with

- 8 -

a white liquor that has a very low sulfidity. Per cent yield is also increased.

The major advantage of this process is the overall reduction of black liquor solids. This reduction is beneficial to present-day Kraft mills that want to increase production but are limited by their recovery system.¹⁴

Irradiation

Another area that is being studied as a possible alternative to Kraft pulping is that of chip irradiation. This process involves the irradiation of chips by electrically-accelerated electrons prior to charging the digester. This is followed by a typical soda or Kraft cook.

The irradiation stablizes the cellulose and hemicellulose molecules and prevents degradation by slowing the peeling reaction of the polysaccharide end groups. This process results in a 5% increase in yield. Losses in bleaching are also reduced due to greater carbohydrate stability.¹⁵

Sulfite - Sulfide Pulping

This process utilizes the same cooking conditions and equipment as Kraft, but the white liquor is a sulfite-sulfide-carbonate solution rather than a sulfide-caustic solution. The sulfitesulfide process results in a 5% increase in yield. The major drawback of this process is the fact that there is not yet a commercial recovery system.¹⁶

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Holopulping

Holopulping consists of two stages. The first stage combines finely chopped wood with an oxidizing agent. The mixture is cooked at a low temperature and pressure. The oxidizing agent modifies the lignin so that it is easily removed in the second stage, which is an alkaline extraction. The main oxidizing agent used is chlorine dioxide, either aqueous or gas. The spent liquor can be burned and the sodium compounds are recoverable; therefore, the level of air pollution is greatly reduced. The per cent yield is 65-80%. The major disadvantage of this process is that a radical change in the design of equipment must be made for both pulping and recover.¹⁷

Chemical - Solvent Pulping

There are several methods of chemical-solvent pulping. The three systems that have drawn the most attention are:

- 1. Hydrotropic pulping
- 2. Alcohol pulping
- 3. Ketone-ammonia pulping

Hydrotropic pulping utilizes hydrotropic salts, such as sodium xylenesulfonate, in a water solution. This solution is added to the chips under typical Kraft temperatures and pressures. This process has not gained acceptance as quickly as was first expected because of the excessive cost of the hydrotropic salts.¹⁸

The second method of chemical-solvent pulping, alcohol pulping, is more practical than the previous method. This process uses mainly methyl alcohol in conjunction with normal Kraft conditions. This process produces a pulp similar to bisulfite pulps with a per cent yield of 52-65%.¹⁹

The third method of solvent pulping is ketone-ammonia pulping. This process involves the use of ketones, such as methyl ethyl ketone, cyclohexanone or acetone in conjunction with aqueous ammonia. The major disadvantages of this process are:

- The pulp must be cooked at 210° C; therefore, the digester equipment must be redesigned.
- 2. The pulp has lower strength than that of Kraft, due to the excessive heat.

The major advantages of ketone-ammonia pulping are:

- 1. Softwood is easily delignified.
- 2. A high per cent yield of 55-68% is possible.
- 3. All the solvents can be recovered.
- 4. Pure lignin can be recovered as a by-product.²⁰

Recently, a great deal of emphasis has been centered around the use of another form of ketone during pulping, that of diketo compounds, commonly referred to as guinones.

QUINONES

Quinones are $\sim \beta$ -unsaturated cyclic diketones of such a structure as they can be converted by reduction into hydroquinones or phenols containing two hydroxy groups. The quinones are highly conjugated and, therefore, are colored. Anthraquinone, for example, is yellow. This conjugated state results in a closely balanced energy level system, which prevents easy conversion to the corresponding hydraquinones.²¹

This unique stability led researchers to experiment with different quinones as a possible additive to soda and Kraft pulps. Some of the types of quinones tested were:

- 1. Benzoquinones
- 2. Napthoquinones
- 3. Anthraquinones

After several preliminary studies, it was found that:

- Benzoquinones had a negative effect on the rate of delignification.
- Napthoquinones had a slightly positive effect on the rate of delignification.
- 3. Anthraquinones had a strongly positive effect on the rate of delignification.²²

Due to the marked improvement of anthraquinones over the other compounds, researchers concentrated their efforts in that area. The second portion of this paper will, therefore, be devoted to this subject. Two anthraquinones have received the most attention. These are:

1. Sodium anthraquinone monosulfate (AMS)

2. 9, 10 anthraquinone (AQ)

Sodium anthraquinone monosulfate was the first compound to be tested. It was thought that the polar, electronwithdrawing group, sulfonate, would be most beneficial to the soda and Kraft processes. Small additions of AMS in a soda cook, 1-2%, resulted in:

- 1. Improved yield
- 2. Reduced amount of rejects
- 3. Accelerated delignification
- 4. No adverse effects on strength
- 5. Stabilization of polysaccharides against alkaline degradation
- 6. Interaction with lignin, which eases its removal. 23

A carbohydrate analysis was made of the soda-AMS cooks. It was found that the soda-AMS pulps yielded a xylan fraction that was equal to that of a normal Kraft cook. A higher value of sugar acids was also present in the soda-AMS pulps. This was due to the oxidation of aldehydic end groups to the corresponding aldonic acid end groups by the quinone. A higher content of glucan implied that significant cellulose retention occurred in the presence of AMS. This increase in retention was due to the stabilization of the cellulose end groups.²⁴

Three different applications for AMS were examined. The

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first was to use AMS in conjunction with alkali as a pretreatment before the actual cook. The second method was to use small amounts of AMS in either a soda or Kraft cook to produce a pulp with a high kappa number. This would then be followed by an oxygen-alkali treatment, which would reduce the pulp to a bleachable grade. The third method proposed the use of hydroquinone followed by the injection of oxygen into the digester at 140° C. the oxygen oxidized the hydroquinone, thereby completing the redox cycle.²⁵

Unfortunately, it was found that the polarity of AMS enhanced the compound's solubility in alkaline pulping liquor. This solubility actually reduced the degree of the positive effects of AMS. This reduction caused the use of AMS at mill scale to be uneconomical.

Attention was then centered on 9, 10 anthraquinone (AQ). AQ is nonpolar and only slightly soluble in alkali. It is, therefore, more effective than AMS.²⁶ AQ has a lower cost and is exceptionally stable during the pulping process.

The acceleration of delignification and the modification of the cellulosic end groups are the primary effects of using AQ in a soda or Kraft cook.

Löwendahl and Samuelson made a detailed study of soda and Kraft cooks designed to prove these effects. A blank Kraft cook was first run. The major end groups produced were two diastereometric 3-deoxyhexonic (metasaccharinic) acids and 2-C-methylglyceric acid. These groups are formed in stopping reactions, which compete with the peeling reaction and are probably also found in glucomannan in wood.²⁷ Trials were then run using 1% and .1% AQ. The proportion of alkaline stopping reaction acids (derived from carboxylic acid end groups formed from reducing sugar end groups in the absence of oxidants) was much lower in the pulp from the 1% AQ cook, while the number of aldonic acid end groups was correspondingly higher. A similar effect was also found at the .1% AQ level, but at a lesser degree. This is because the presence of sulfide is the important factor at low AQ levels. It is the presence of these aldonic acid end groups that supports the conclusion that AQ is first consumed by lignin reactions and is then regenerated by oxidation.²⁸ These results show that in competition with the alkaline-peeling and alkaline-stopping reactions occur in all types of alkaline pulping, oxidation of the reducing terminal sugar groups is one of the most important reactions during oda and Kraft pulping.

Löwendahl and Samuelson concluded that the stabilization of the carbohydrates against alkaline peeling by oxidation of reducing end groups to aldonic end groups and the catalyzed delignification of cellulose are greatly affected by the addition of AQ. It can, therefore, be assumed that the observed increase in yield, at a given kappa number, is a result of the above reactions.²⁹

Advantages produced by the addition of AQ are:

1. Lower required cook temperature

2. Lower chemical demand

3. Lower energy demand

4. Improved pulp quality.³⁰

Another advantage of AQ is that it is not corrosive or explosive; therefore, no special equipment is necessary.

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Researchers are currently attempting to determine the best method of AQ to a mill operation. Presently, the use of AQ is restricted to mills using the soda process, or those mills that are under Environmental Protection Agency (EPA) pressure to switch from Kraft to soda. AQ has been handled on a large commercial scale without difficulty for many years, and at this time does not appear to be a pollutant.

Holton and Chapman had a great deal of success with a mill trial in which they injected varying levels of AQ directly into the digester. They found that at a given AQ level, the actual kappa number fell as much as 30 units and averaged 18 units below predicted levels.³¹

Holton determined that a reduction in active alkali in the presence of AQ would result in a pulp of a normal kappa number. Except for this obvious advantage of reduction of active alkali, the effects of AQ are not easily seen unless reference can be made to the reduction in the H factor. A reduction of approximately 30% resulted with the addition of AQ. This reduction in H factor allows the lowering of the maximum cook temperature. This reduction in temperature yields large energy savings.³²

The great effects of AQ on the kappa number and H factor were probably due to the build up of AQ in the system. It was found that when the addition of AQ to the digester was stopped, enough AQ was retained in the system to allow at least one more cook to have a lower kappa number. The AQ was retained in the system because of the recirculation of black liquor. Holton suggested that the level of AQ actually needed may be much less than that used in their trial.

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The pulp produced from the trial was used to make linerboard. There was no difference in the amount of refining energy required, quality of the board or in machine runability. Holton concluded that in order to achieve the maximum efficiency of AQ, intermediate reductions in alkali concentration, cook time and maximum temperature should be made.³³

There is one fact about AQ that no one wants to discuss. This is the fact that AQ is carcenogenic. The qualifying toxic oral dose to rats and the lowest published toxic dose is 90g/kg 190 DC. The principle form of cancer produced by AQ is tumors, which are introduced to the major organs.³⁴ Gloves, masks and aprons should be used when handling AQ. The FDA has not yet approved the use of AQ in food board, but a ruling is expected to be made within two years.

EXPERIMENTAL OBJECTIVES

This experiment was designed to demonstrate two theoretical advantages of adding AQ to a Kraft cook.

One, the per cent yield of a Kraft cook modified by the addition of AQ would be greater than that of an unmodified Kraft pulp at a constant Kappa number.

The second was to determine if the strength of hardwood would be improved by the addition of AQ.

MATERIALS AND EQUIPMENT

- 1. Popel chips
 - a. Supplied by the S. D. Warren Company. b. Hand sorted to insure chip uniformity and quality.
- 2. White liquor composition (NaOH + Na₂S)
 - 17% sulfidity a.
 - b. Total alkali = 91.45 g/l
 - c. Active alkali = 89.9 g/l
 - NaOH (as Na₂O) = 74.4 g/lNa₂S (as Na₂O) = 15.5 g/ld.
 - e.
- 3. 9,10-anthraquinone (Figure 1.)
- 4. M & K digester
- 5. Waring blender
- 6. Sidehill screen
- 7. Modified wine press
- 8. Plastic bags with ties
- PFI mill 9.
- Noble and Wood sheet mold and wires 10.

PROCEDURE

Popel chips supplied from S. D. Warren were hand sorted in order to insure a uniform size and quality for all ten trials. 675 O.D. chips were charged to the M & K digester. White liquor at 17% sulfidity was added to the digester. The total liquid to wood ratio was 5/1, with an actual Na₂O charge of 20%. The chips were cooked at 160[°]C for various lengths of time (Figure 2). Trials 1-6 were completed before Trials 7-10 were initiated. Trials 1-6 were used as the basis for determining the digester conditions for Trials 7-10.

At the completion of the cook, the chips were removed from the digester, rinsed and defibered for one minute in a Waring blender. The pulp was then thoroughly washed on a sidehill screen. Per cent yield and Kappa number were then determined.

The pulp was stored in an airtight plastic bag. The pulp was refined in the PFI mill at 0, 5,000, 10,000 and 15,000 revolutions. Standard Noble and Wood handsheets were made at all four levels of revolutions. The handsheets were stored in the constant humidity room until they were tested. The strength tests used to test the handsheets were: tear, tensil, mullen and fold.

After the results of Trials 1-6 were evaluated, conditions for Trials 7-10 were then determined. Trials 7-10 were performed in the same manner as were the previous trials.

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RESULTS

Trials 7-10 were run at 0.05% AQ because the reduction in Kappa number at this level was comparable to that of the 0.1% and 0.5% levels (Figure 3). Although the Kappa number was further reduced at the 1.0% level, the expense of AQ at this level was not economically justifiable. Also, in most of the literature on current mill operations, 0.05% AQ is the level being charged to the digester.

It was found that the per cent yield decreased as much as ten points as the level of AQ was increased (Figure 3). Unfortunately, the Kappa numbers did not decrease as much as was expected. Rather, the Kappa number for Trials 1-6 dropped only a maximum of two points from the unmodified reference point (Figures 4 and 5). One observes that an extrapolated graph of per cent yield versus per cent AQ, at a constant Kappa number, would show that the unmodified Kraft cook would have a greater per cent yield than the modified cooks. The literature claims that a significantly reduced Kappa number accompanies the decrease in per cent yield. The reduction in Kappa number, therefore, allows for a shorter cook time and lower chemical demand that will produce a pulp of equal quality to that of unmodified Kraft. The results of this experiment did not support the above claims.

There are several explanations for these differences in results:

 The facilities utilized in the literature recycled the black liquor. This allowed for a build up of AQ in the system, so that in actuality, the researchers were using an effective AQ charge of anywhere from 0.05% to over 1%.

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- The pulp samples that were tested in this experiment were so small that minor changes in moisture would greatly affect the results.
- The M & K digester does not have good circulation. Channelling does occur, which can result in a nonuniform pulp.

It was found that the addition of 0.05% AQ increased the mullen and tear strengths of the pulp (Figures 6 & 7). This is readily seen as one studies the zero revolution curve for both tests. The increase in strength is due solely to the addition of AQ. The tensil strength did not show improvement until the sample was refined. 10,000 revolutions resulted overall in the strongest pulps (Figures 8 & 9).

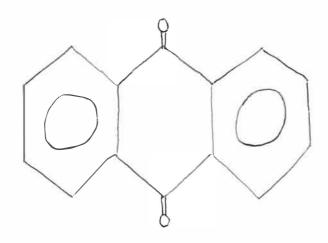
Trials 7-8, which were cooked for 30 and 60 minutes respectively, resulted in strong bleachable pulps. but the Kappa numbers were much higher than that of the unmodified Kraft cook. But the per cent yield was not as high as was needed to be competitive with the unmodified cook. On a larger scale operation that would recycle the AQ, a lower Kappa number would be possible; thereby, making a reduction in the cook time possible.

Trials 9 and 10, which were cooked at 30 and 60 minutes respectively, were charged with only 10% Na₂O on the chips. This resulted in a very raw cook with an extremely high Kappa number. The pulp had good strength, but only after a high degree of refining (Figure 10). AQ might possibly be used as an additive to high yield pulps.

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CONCLUSION

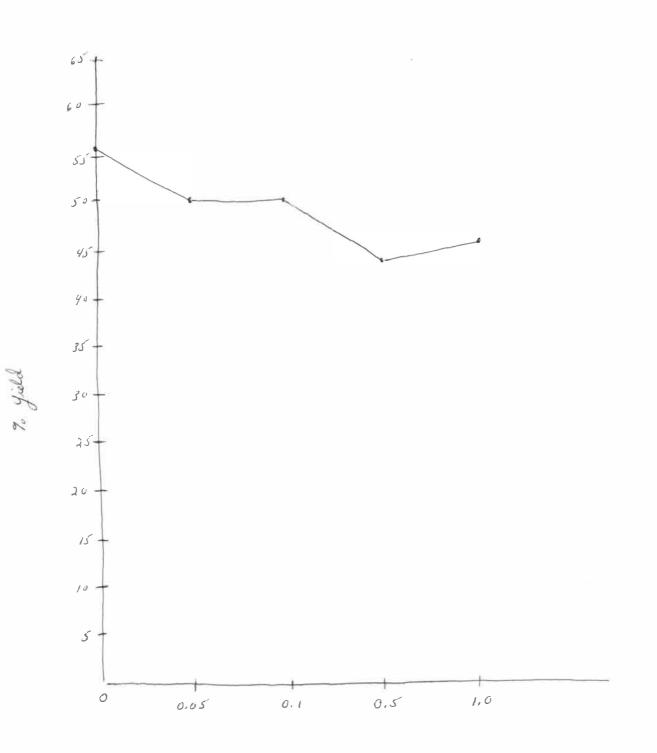
This experiment does not support the claim that higher per cent yields and lower Kappa numbers are obtainable with low amounts of AQ. Increased pulp strength is possible with the addition of 0.05% AQ. Reduction in time and chemical requirements may be possible, but only on a large scale operation, which recycles the black liquor, resulting in a build up of anthraquinone. 9,10 - ANTHRAQUINONE



CONDITIONS OF TRIALS

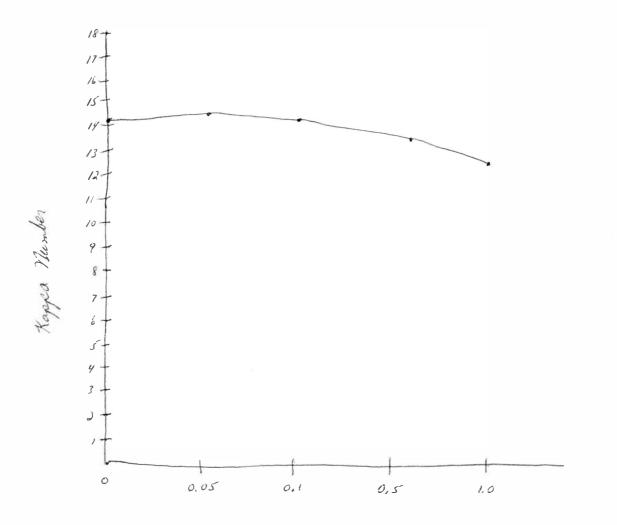
TRIAL	TI	ME	8AQ	<u>% Na₂0 (on chips)</u>
1	90	min.	0	20
2	150	min.	0	20
3	90	min.	0.05	20
4	90	min.	0.10	20
5	90	min.	0.50	20
6	90	min.	1.00	20
7	30	min.	0.05	20
8	60	min.	0.05	20
9	30	min.	0.05	10
10	60	min.	0.05	10

% YIELD - VS - % AQ



% AQ

KAPPA NUMBER - VS - % AQ

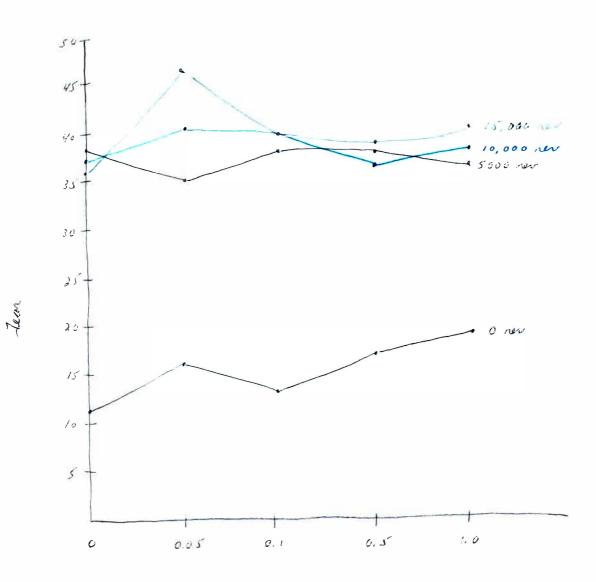


9. AQ

% YIELD AND KAPPA NUMBER

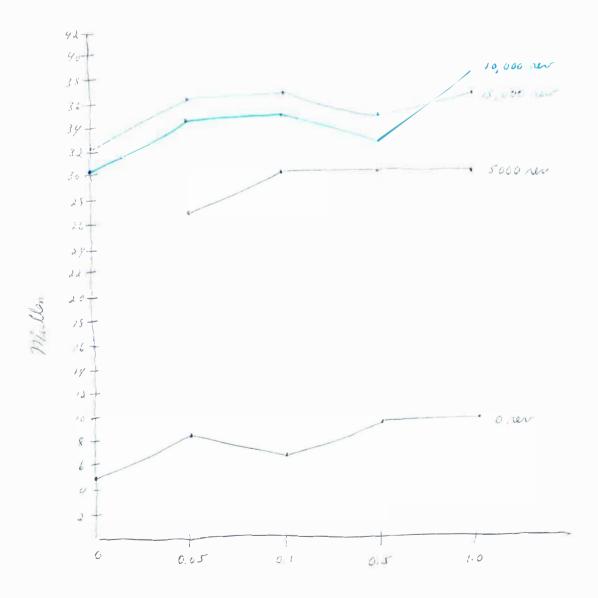
TRIAL	8 YIELD	KAPPA NUMBER
1	55.2	14.03
2	44.7	13.5
3	50.8	14.7
4	50.6	14.29
5	44.59	13.89
6	45.7	12.89
7	51.8	18.62
8	56.3	18.3
9	68.6	68.52
10	71.2	62.75

TEAR - VS - % AQ



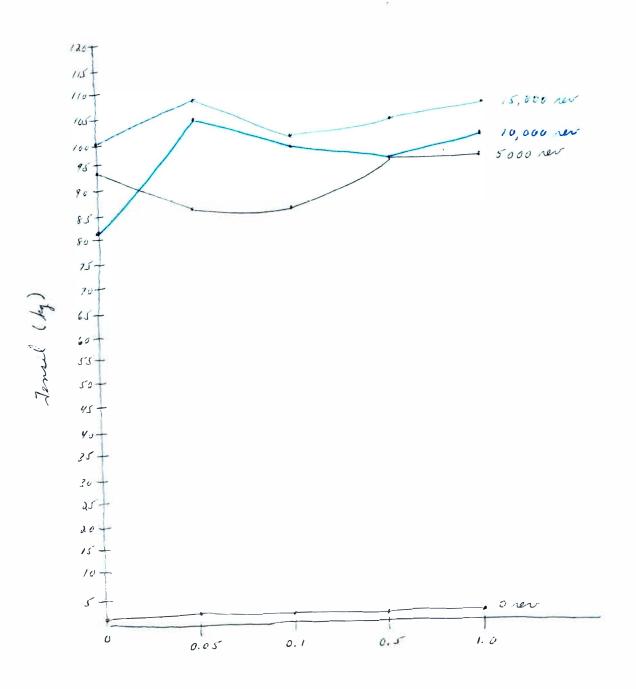
% AQ

MULLEN - VS - 8 AG



9. AQ

TENSIL - VS - % AQ



9. AQ

STRENGTH COMPARISON

TRIAL	BASIS	CALIPER	BULK R	TEAR	TENSIL	MULLEN
1-0	37.9	6.8	0.326	12	0.0506	5.2
5000	39.9	4.9	0.480	38	94.9	40.1
10000	39.3	4.9	0.479	37	81.5	30.8
15000	40.8	5.1	0.471	36	100.4	32.2
2 0	20.0	C D	0.040			7 0
2-0	39.9	6.9	0.340	16.5	0.0658	7.3
5000	39.9	5.3	0.441	29.5	84.4	27.3
10000	40.9	5.3	0.459	41	105	34.8
15000	40.5	5.2	0.457	41	106	33.4
3-0	37.7	6.9	0.321	16	0.0631	8.4
5000	39.5	5.3	0.438	35	87.6	28.1
10000	38.9	5.1	0.451	40	102.8	35.1
15000	41.7	5.2	0.472	47	109.7	36.1
4-0	39.1	6.8	0.339	14	0.0673	6.9
5000	39.9	5.3	0.441	38	87.5	30.2
10000	39.7	5.0	0.440	36	99.4	35.6
15000	39.9	5.0	0.469	40	99.0	37.1
5-0	20 F	C D	0.344	17	0 0705	9.1
	39.5	6.8		17	0.0705	
5000	40.7	5.3	0.471	38	96.3	30.7
10000	40.1	5.1	0.463	37	96.0	33.1
15000	39.5	5.1	0.459	38	104	35.0
6-0	39.1	6.7	0.343	19	0.0693	9.3
5000	40.5	5.4	0.440	36	96.3	30.6
10000	40.3	5.2	0.457	38	103.3	38.8
15000	41.7	5.3	0.461	42	107.6	37.8

Figure 10

STRENGTH COMPARISON

TRIAL	BASIS	CALIPER	BULK R	TEAR	TENSIL	MULLEN
7-0	42.9	8.0	0.3196	24	28.6	13
5000	39.7	5.9	0.3782	46.7	43.3	35.2
10000	40.8	5.5	0.4391	61.3	107.2	46.5
15000	40.2	5.2	0.4550	65.3	116.6	51.2
				04.0		0.1
8-0	40.2	6.9	0.3432	24.0	26.6	8.1
5000	42.4	5.6	0.4451	58.7	126.8	47.0
10000	42.1	5.3	0.4646	64.0	110.4	54.7
15000	40.6	4.9	0.4883	66.0	117.0	57.8
0 0	41 0	0.6	0 0571		15 0	
9-0	41.8	9.6	0.2571	26.7	15.8	1.5
5000	42.5	5.8	0.4317	50.7	127.5	53.9
10000	41.6	5.7	0.4293	54.7	89.9	50.3
15000	40.9	5.3	0.4521	61.3	103.9	54.4
10-0	42.9	11.1	0.2300	25.3	22.9	3.5
5000	39.6	4.7	0.4966	44.0	92.1	53.7
10000	40.3	5.1	0.4675	40.0	71.9	52.9
15000	40.7	4.8	0.4982	42.7	72.3	53.6

FOOTNOTES

- ¹ Sjöström, <u>The Behavior of Wood Polysaccharides During</u> <u>Alkaline Pulping Processes</u>, TAPPI, Vol. 60, No. 9, <u>Sept. 1977, pp. 151.</u>
- ² <u>The</u> <u>Pulping of Wood</u>, Ronald G. MacDonald, ed., McGray-Hill Book Company, New York, 1969, pp. 370.
- ³ Holton, H. H., <u>Soda Additive in Softwood Pulping: A Major</u> <u>New Process, Pulp & Paper Canada, Vol. 78, No. 10,</u> <u>T218-T222, October 1977, pp. 1.</u>
- ⁴ Lowe, Kenneth E., <u>Is Pulping Technology on</u> the <u>Verge of a</u> Revolution?, Pulp & Paper, July 1974, pp. 53.
- ⁵ Ibid., pp. 54.
- ⁶ Oxygen Pulping of Hardwood, TAPPI, Vol. 60, No. 11, Nov. 1977, pp. 40-41.
- ⁷ Lowe, op. cit., pp. 54.
- ⁸ Oxygen Pulping of Hardwood, op. cit., pp. 40.
- ⁹ Lowe, op. cit., pp. 54-55.
- ¹⁰ Brink, D. L., <u>Pulping Process Studies</u>. Aspects of an <u>Integrated</u> <u>Nitric Acid Pulping Process</u>, TAPPI, Vol. 44, No. 4, April <u>1961</u>, pp. 257.
- Alkaline Pulping With Amine, TAPPI, Vol. 60, No. 11, Nov. 1977, pp. 39-40.
- ¹² Ibid., pp. 41.
- ¹³ Lowe, op. cit., pp. 53.
- ¹⁴ Ibid., pp. 53.
- ¹⁵ Ibid., pp. 53-54.
- ¹⁶ Ibid., pp. 55.
- ¹⁷ Ibid., pp. 55-56.
- ¹⁸ Ibid., pp. 56.
- ¹⁹ Ibid., pp. 56.
- ²⁰ Ibid., pp. 56.

- ²¹ Morrison, Robert Thornton, and Robert Neilson Boyd, Organic Chemistry, Allyn & Bacon, Inc., Boston, 1973, pp. 878.
- ²² Lowe, op. cit., pp. 2.
- ²³ Ghosh, K. L., V Venkatesh, W. J. Chin, and J. S. Gratzl, <u>Quinone Additives in Soda Pulping of Hardwood</u>, TAPPI, Vol. 60, No. 11, Nov. 1977, pp. 127.
- ²⁴ Ibid., pp. 130.
- ²⁵ Ibid., pp. 127.
- ²⁶ Holton, op. cit., pp. 1.
- ²⁷ Löwendahl, Lars and Olaf Samuelson, <u>Carbohydrate Stabilization</u> <u>During Soda Pulping With Addition of Anthraquinone, TAPPI,</u> <u>Vol. 61, No. 2, Feb. 1978, pp. 19.</u>
- ²⁸ Ibid., pp. 20.
- ²⁹ Ibid., pp. 20.
- ³⁰ Holton, H. H., and F. L. Chapman, <u>Kraft Pulping With Anthra-</u> quinone, TAPPI, Vol. 60, No. 11, Nov. 1977, pp. 121-122.
- ³¹ Ibid., pp. 121.
- ³² Ibid., pp. 124.
- ³³ Ibid., pp. 123.
- ³⁴ <u>Registry of Toxic Effects of</u> <u>Chemical Substances</u>, Herbert E. Christensen, ed., U. S. Department of Health, Education and Welfare, Rockville, Maryland, June 1976, pp. 117.

BIBLIOGRAPHY

- Alkaline Pulping With Amine, TAPPI, Vol. 60, No. 11, November 1977, pp. 39-40.
- Brink, D. L., <u>Pulping Process Studies</u>. Aspects of <u>an Integrated</u> <u>Nitric Acid Pulping Process</u>, TAPPI, Vol. <u>44</u>, No. 4, April <u>1961</u>, pp. 256-62.
- Evans, John C., <u>Pulping, Bleaching, Recovery Are Covered in</u> <u>Varied Technical Programs</u>, Pulp & Paper, January 1978, pp. 142.
- Ghosh, K. L., V. Venkatesh, W. J. Chin, and J. S. Gratzl, <u>Quinone Additives in Soda Pulping of Hardwood</u>, TAPPI, Vol. 60, No. 11, Nov. 1977, pp. 127-131.
- Holton, H. H., and F. L. Chapman, <u>Kraft Pulping With Anthra-</u> <u>quinone</u>, TAPPI, Vol. 60, No. 11, Nov. 1977, pp. 121-125.
- Holton, H. H., Soda Additive in Softwood Pulping: A Major New Process, Pulp & Paper Canada, Vol. 78, No. 10, T-218-T222, Oct. 1977, pp. 1-4.
- Kenig, S., Treatment of Lignocellulosic Material in an Alkaline Pulping Liquor Containing Anthraquinone Sulfonic Acid Followed by Oxygen Delignification, U. S. Pat. 3,888,727, June 10, 1975.
- Lowe, Kenneth E., <u>Is</u> <u>Pulping Technology on</u> the Verge of a <u>Revolu-</u> <u>tion?</u>, Pulp & Paper, July 1974, pp. 52-56.
- Löwendahl, Lars, and Olaf Samuelson, Carbohydrate Stabilization During Soda Pulping With Addition of Anthraquinone, TAPPI, Vol. 61, No. 2, Feb. 1978, pp. 19-21.
- Morrison, Robert Thornton and Robert Neilson Boyd, Organic Chemistry, Allyn & Bacon, Inc., Boston, 1973, pp. 878, 992-994.
- Oxygen Pulping of Hardwood, TAPPI, Vol. 60, No. 11, Nov. 1977, pp. 40-41.
- The Pulping of Wood, Ronald G. MacDonald, ed., Vol. 1, McGraw-Hill Book Company, New York, 1969, pp. 370.
- Registry of Toxic Effects of Chemical Substances, Herbert E. Christensen, ed., U. S. Department of Health, Education and Welfare, Rockville, Maryland, June 1976.
- Sjöström, Eero, <u>The Behavior of Wood Polysaccharides During</u> Alkalin Pulping Processes, <u>TAPPI</u>, Vol. 60, No. 9, Sept. 1977, pp. 151-154.

- <u>Suspected Carcenogens</u> <u>A</u> <u>Subfile of the NIOSH Toxic Substances</u> <u>List</u>, Herbert E. Christensen, ed., U. S. Department of Health, Education and Welfare, Rockville, Maryland, June 1975.
- Worster, H. E., McCandless, D. L., <u>Pretreatment of Lignocellu-</u> losic Material With Anthraquinone Salts in Alkaline <u>Pulping</u>, Canada pat. 986,662, April 6, 1976.