Repulping wet-strength paper

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ABSTRACT

A new repulping process that uses a nonchlorinated oxidizing agent and a rewetting agent was found to be very effective in repulping wet-strength paper that was difficult to break down. The process is particularly useful in repulping unbleached paper and old corrugated containers (OCC) containing polyaminoamide-epichlorohydrin (PAE) wet-strength resins. The process involves oxidizing the wet-strength paper at a low pH with inorganic or organic peroxides followed by hydrolyzing the wet-strength paper at a high pH. In field trials, unbleached paper containing high levels of PAE resins was repulped to about 95% in mill hydropulpers. This process enables papermakers to defiber unbleached paper and OCC more efficiently than commonly practiced neutral or alkaline repulping processes.

FIBER FROM RECYCLED PAPER IS AN important raw material source that offers several economic advantages to the paper manufacturer. The papermaker can reduce raw material costs by blending secondary fibers with virgin fibers and by reusing their broke and clippings instead of discarding them in solid waste landfills. As the demand for secondary fiber increases, paper made with permanent wet-strength resins, such as polyaminoamide-epichlorohydrin (PAE), becomes an important source of fiber. However, these papers, particularly unbleached paper and old corrugated containers (OCC), are difficult to repulp. Sodium hypochlorite is commonly used in repulping bleached wet-strength paper, but its inability to completely repulp unbleached wet-strength paper and environmental regulations reducing adsorbable organic halogen (AOX) effluent discharges from paper mills limit its use *(1–3).*

Peroxydisulfate ($M_2S_2O_8$) and potassium peroxymonosulfate ($KHSO_5$, the active component in the triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) are reported to be effective repulping reagents for wet-strength bleached paper, but they are less effective on unbleached and OCC wet-strength papers when used in conventional neutral or alkaline repulping processes *(2, 3).* Undesirable side reactions between oxidants and lignin make unbleached paper difficult to repulp. Oxidants that decompose to free radicals can abstract hydrogen from lignin to form nonreactive radicals *(4),* leaving, for the most part, an unoxidized wet-strength resin. The side reactions can be overcome with excess oxidant *(5),* but this is expensive, inefficient, and harmful to the fibers.

The chemistry of inorganic and organic peroxides has been extensively studied and finds importance in reduction–oxidation and polymerization processes. Under proper reaction conditions, the oxidant is activated by metals or is thermally decomposed to form free radicals. The highly reactive radicals can abstract hydrogen or other atoms from saturated and unsaturated substrates, add to unsaturated substrates, combine or dimerize with other free radicals, or undergo reduction–oxidation reactions involving electron and ligand-transfer processes *(6–8).* Substrates such as polyhexamethylene adipamide (Nylon-6,6), a linear polyamide similar to the PAE backbone, are oxidized by a hydrogen peroxide–iron redox couple (Fenton's reagent) *(9).*

Oxidants catalyzed by metal–ligands are reported to cleave polypeptides by oxidation followed by a nucleophilic attack on the oxidized substrate with amines *(10).* The reactions between hydroxyl radicals from hydrogen peroxide and model compounds representing phenolic and nonphenolic nuclei in lignins were found to be dependent on reaction pH *(11).* The above studies suggest that free radicals may effectively repulp unbleached wet- strength paper under conditions that favor the free radical–wet-strength resin reaction and not the free radical–lignin reaction.

In this study, repulping of wet-strength paper with inorganic oxidants was investigated in the laboratory. The effect of process pH, time, temperature, rewetters, shear, and reactant concentration was related to repulping. The degree of repulping was quantitatively determined by filtering the repulped paper through a slotted vibrating screen having 0.15-mm openings. Dry tensile strengths of handsheets made from repulped paper are reported and compared to handsheets made from virgin fibers. The performance of the new repulping process was compared to alkaline processes on repulping unbleached linerboard at different paper mills.

EXPERIMENTAL

Repulping procedures

Alkaline process. Commercial paper was cut into 1-in. x 1-in. pieces and diluted to a weight ratio of 2% in tap water containing less than 0.15 ppm iron and 0.30 ppm copper. The pH was adjusted to 11 with aqueous sodium hydroxide before heating to a desired reaction temperature (i.e.,

Paper	Wet-strength resin in paper, %
Unbleached linerboard (A)	0.6
Unbleached linerboard (B)	0.4
Unbleached linerboard (C)	1.0
Bleached poster board (D)	1.0
Unbleached seedling paper (E)	1.0
Unbleached raisin tray paper (F)	1.0

I. Commercial paper used in the repulping study. All paper samples were made with a PAE wet-strength resin except for B, which was made with a polyamine-epichlorohydrin resin.

Reagent	Percent reagent on paper	Process pH	Repulping time, min	Percent repulped
Unbleached linerboard (A)				
NaOH	7.0	11	60	50
$Na_2S_4O_8$	1.0	11	60	66
$KHSO_5$	1.0	11	60	66
$KHSO_5$ + 0.1% rewetter on paper	5.0	11	60	67
Unbleached linerboard (B)				
NaOH	7.0	11	60	64
$Na_2S_4O_8$	10.0	11	60	74
$KHSO_5$	10.0	11	60	77
NaOCl	10.0	6	60	15
Unbleached linerboard (C)				
NaOH	7.0	11	60	32
$Na_2S_4O_8$	10.0	11	60	58
$KHSO_5$	10.0	11	60	61
Bleached poster board (D)				
NaOH	7.0	12	60	48
$Na_2S_4O_8$	2.5	11	60	56
$KHSO_5$	2.5	12	60	58

II. Alkaline repulping of bleached and unbleached paper containing PAE and polyamine-epichlorohydrin wet-strength resins. Repulping temperature was 70°C. The paper was sheared for 3 min at 3000 rpm after treatment with reagents. The pH was adjusted to 11 by adding NaOH.

70–90°C) while gently stirring the paper. The oxidant was added and, if needed, the pH was readjusted to 11 with more sodium hydroxide. Then the paper was mixed a minimum of 60 min at reaction temperature. The paper mixture was transferred to a disintegrator (TAPPI Test Method T 205 om-88) and sheared for several minutes at 3000 rpm. A sample of the pulp was filtered for 20 min through a vibrating slotted screen having 0.15-mm openings, and the residuals (unpulped paper) were dried at 105°C.

Two-pH process. Commercial paper was cut into 1-in. x 1-in. pieces and diluted to a weight ratio of 2% in tap water containing less than 0.15 ppm iron and 0.30 ppm copper. A rewetter was optionally added, and the pH was adjusted to between 3 and 7 with a mineral acid before heating to a desired reaction temperature (i.e., 70–90°C) while gently stirring the paper. The oxidant was added, and mixing continued for at least 30 min at reaction temperature. The pH was adjusted to about 11 with aqueous sodium hydroxide and mixed for a least another 30 min at reaction temperature. The paper mixture was transferred to a disintegrator (TAPPI Test Method T 205 om-88) and sheared for several minutes at 3000 rpm. A sample of the pulp was filtered for 20 min through a vibrating slotted screen having 0.15-mm openings, and the residuals (unpulped paper) were dried at 105°C.

Handsheet procedure

Four-gram handsheets were made with an 8-in. Mark IV dynamic handsheet mold using laboratory recycled and virgin furnishes (0.5% consistency) adjusted to pH 7. The wet handsheets were pressed with a hand roller between felt, dried for 10 min at 105°C on a Williams dryer, and oven cured on a wire rack for 10 min at 105°C. Dry tensile strengths of the handsheets were measured on an Instron tester.

DISCUSSION

The papers for this study were obtained from various mills in the United States and are listed in **Table I.** The paper samples contain either PAE or polyamine-epichlorohydrin wet-strength resins. The amount of wet-strength resin in the paper was provided by the mills. Papers C–F were also sized with 0.1–0.2% alkyl ketene dimer (AKD). The wet strength (% wet/dry) of the papers was greater than 20% in every case.

The paper was treated at specified temperatures and pH with reagents in a closed-head stainless steel container using gentle mixing from a three-blade marine propeller. The oxidants were added on actives except for peroxymonopersulfate ($KHSO_5$ or MPS), which was added as the triple salt mixture. Mixing during the repulping experiments was carefully controlled to augment the performance of the reagents used in the process. After treatment, the paper mixture was subjected to high shear in a disintegrator for 3 min (A–D) or 6 min (E, F) at 3000

rpm. Papers E and F required more shear to completely defiber, possibly due to a high level of AKD in the paper.

Alkaline repulping

Repulping at pH 11 was ineffective on unbleached and bleached paper containing permanent wet-strength resins (PAE or polyamine-epichlorohydrin) despite the type and amount of oxidizing agent used (**Table II**). Sodium hypochlorite was used as an oxidizing agent to repulp unbleached paper B, the paper containing the lowest dose of wet-strength resin (0.4%) in this group, and because of its poor results, sodium hypochlorite was not included in any more testing. A propoxylated linear alcohol (rewetter) was added to lower the surface tension of the repulping liquor (from 60 to 28 dynes/cm) to improve paper A wetting, but this did not improve repulping. The reagents were also ineffective in repulping a bleached poster board (D) containing 1.0% PAE resin and AKD sizing agent.

Two-pH repulping

Repulping the same paper samples (A–D) by first heating with an oxidizing agent at pH ≤ 7 for 30 min and then raising the pH to 11 and heating for an additional 30 min resulted in significantly higher paper repulping (**Table III**). In all cases, the same level or a reduced level of oxidizing agent achieved higher degrees of repulping compared to the pH 11 alkaline process. Although lignin can be oxidized over a wide pH range, it appears from these results that the oxidant–wet-strength resin reaction (or oxidant–cellulose reaction) is favored over the oxidant–lignin reaction at a low pH. Further analysis is required to determine the oxidized substrate (wet-strength resin, cellulose, or both) and the mechanism of oxidation (free radical, nucleophilic, or electrophilic addition of peroxide anions and cations) *(12–14)* during repulping wet-strength paper with inorganic peroxides.

Reagent	Percent reagent on paper	Process pH	Repulping time, min	Percent repulped
		Unbleached linerboard (A)		
$Na_2S_4O_8$	1.0	4/11	60	79
$KHSO_5$	1.0	4/11	60	75
H_2O_2	1.0	4/11	60	75
		Unbleached linerboard (B)		
H_2O_2	1.0	4/11	60	87
H_2O_2	5.0	4/11	60	87
$KHSO_5$	10.0	4/11	60	88
		Unbleached linerboard (C)		
$Na_2S_4O_8$	10.0	3/11	60	74
$KHSO_5$	2.5	3/11	60	70
$KHSO_5$	10.0	3/11	60	89
H_2O_2	10.0	3/11	60	84
		Bleached poster board (D)		
$Na_2S_4O_8$	2.5	7/11	60	94
$KHSO_5$	2.5	7/11	60	89
H_2O_2	2.5	7/11	60	88

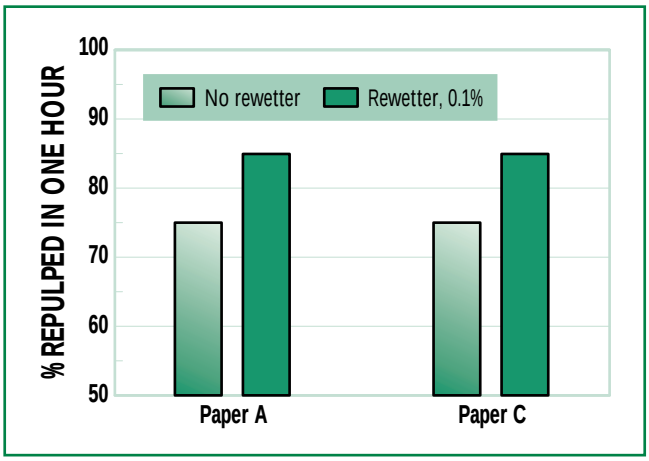
III. Two-pH repulping of bleached and unbleached paper containing PAE and polyamine-epichlorohydrin wet-strength resins. Repulping temperature was 70°C. The paper was processed at the lower pH for 30 min before increasing the pH with NaOH. The paper was sheared for 3 min at 3000 rpm after treatment with reagents.

Reagent	Percent reagent on paper	Percent rewetter on paper	Process pH	Repulping time, min	Percent repulped
			Unbleached linerboard (A)		
$Na_2S_4O_8$	1.0	0.10	4/11	60	80
$KHSO_5$	1.0	0.10	4/11	60	84
H_2O_2	1.0	0.10	4/11	60	82
H_2SO_4 - NaOH	9.0	0.10	4/11	60	70
			Unbleached linerboard (C)		
$KHSO_5$	2.5	0.10	3/11	60	77
$KHSO_5$	2.5	0.15	3/11	60	79
H_2SO_4 - NaOH	9.0	0.10	3/11	120	45

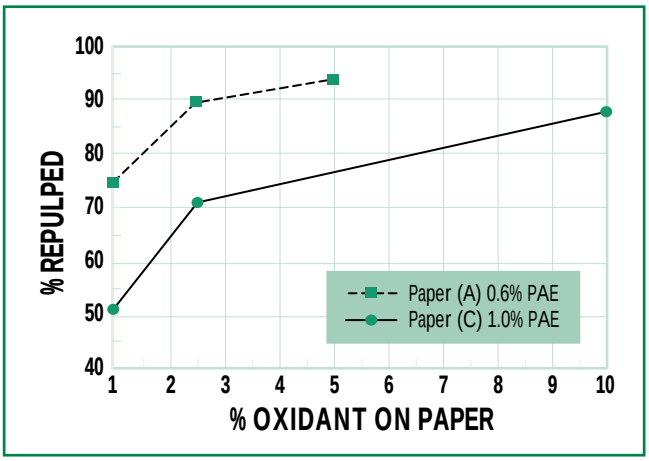
IV. The effect of a rewetter in the two-pH repulping of unbleached paper containing PAE wet-strength resins. Repulping temperature was 70°C. The paper was processed at the lower pH for 30 min before increasing the pH with NaOH. The paper was sheared for 3 min at 3000 rpm after treatment with reagents.

Oxidation of wet-strength resins

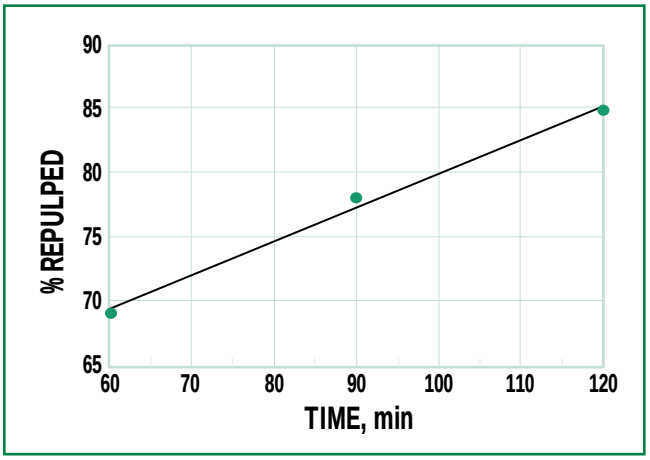
PAE. The polyaminoamide-epichlorohydrin resin contains secondary amides and tertiary amines that are susceptible to oxidation. Oxidation of tertiary amines is discussed in the next section. Oxidation of secondary amides (i.e., amides on the backbone of the PAE resin) by a free radical pathway proceeds by a



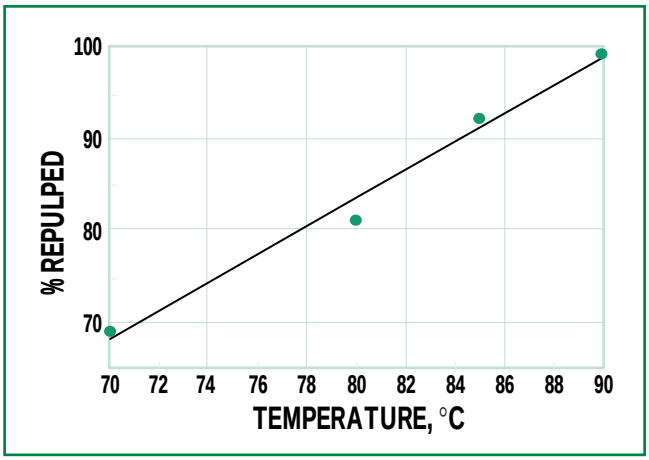
1. Effect on rewetter on two-pH repulping (2.5% MPS, 70°C)



2. Effect of oxidant level on two-pH repulping (MPS, repulped for 1 h, 70°C)



3. Effect of process time on two-pH repulping (2.5% MPS, 0.1% rewetter, paper C, 70°C)



4. Effect of process temperature on two-pH repulping (2.5% MPS, 0.1% rewetter, paper E, repulped for 2 h)

free radical attack on the carbon alpha to the amide nitrogen, which is activated by the electron pair on the nitrogen. This is followed by the resin decomposition reaction (C-N fission), resulting in primary amide and aldehyde byproducts *(15, 16)*. To confirm this mechanism, an aqueous solution of commercial PAE resin was reacted with a hydrogen peroxide–iron redox couple (Fenton's reagent) at pH 4 and 50°C. An aldehyde byproduct and chemical shifts in the amide structure were observed in ^{13}C NMR spectra of the treated PAE solution, suggesting that oxidation by a free radical mechanism is plausible.

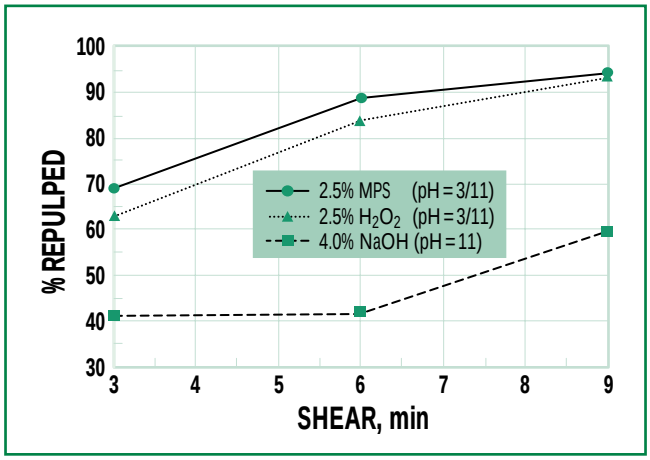
Polyamine-epichlorohydrin. This resin has oxidizable secondary and tertiary amine groups. The most probable path of oxidation is a nucleophilic attack by the amines in the resin on an electrophile (i.e., peroxide cations or free radicals), forming amine oxides. Cleavage follows, producing alkenes and hydroxylamines (the Cope Elimination Reaction) *(17)*.

Two-pH repulping with a rewetter

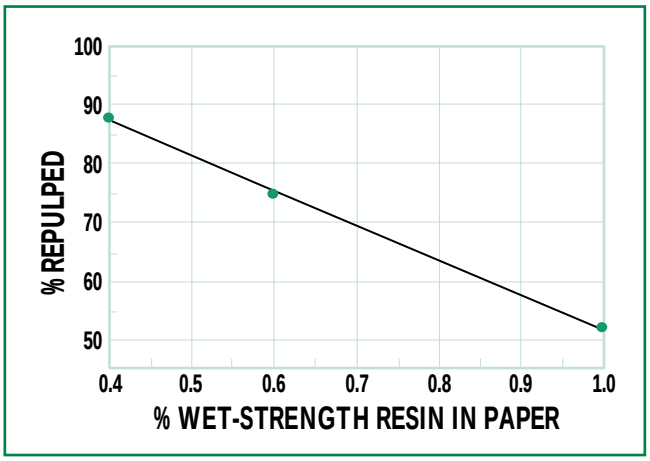
Although a rewetter did not affect the degree of repulping for unbleached paper A with the alkaline process, the same rewetter used in the two-pH process increased the overall degree of repulping (**Table IV** and **Fig. 1**). Complete wetting of the paper allowed the oxidant to penetrate from the surface into the paper. This resulted in a more uniform oxidation of the substrate (PAE resin and/or cellulose), and consequently, higher degrees of repulping were achieved. Rewetters are surfactants that effectively decrease the time it takes to wet the paper by lowering the surface tension of the repulping liquor. For a rewetter to be effective, it must reduce the surface tension of the repulping liquor to less than 30 dynes/cm and not create foam during high shearing of the paper. Rewetters are typically linear or branched ethoxylated or propoxylated alcohols. Defoamers can also work as rewetters; examples are silicone-based emulsions.

Optimum process conditions for the two-pH process

The effects of oxidant level, process time, process temperature, shear, and the level of wet-strength resin on repulping unbleached paper by the two-



5. Effect of shear on two-pH repulping (0.1% rewetter, paper E, repulped for 2 h, 70°C)



6. Effect of wet-strength resin dose on two-pH repulping (1.0% H_2O_2, repulped for 1 h, 70°C)

Paper	Reagent	Percent reagent on paper	Percent rewetter on paper	Process temp., °C	Process pH	Process time, min	Shear at 3000 rpm, min	Percent repulped
A	$KHSO_5$	2.5	0.1	70	4/11	90	3	89
B	$KHSO_5$	2.5	0.1	70	4/11	90	3	85
C	$KHSO_5$	2.5	0.1	70	4/11	120	3	85
D	$Na_2S_4O_8$	2.5	-	70	7/11	60	3	94
E	$KHSO_5$	2.5	0.1	85	4/11	120	6	98
F	$KHSO_5$	3.0	0.1	85	3/11	120	6	96

V. Optimized laboratory conditions for repulping papers A–F by the two-pH process. The paper was processed at the lower pH for at least 30 min before increasing the pH with NaOH.

pH process are illustrated in Figs. 2–6. All these factors greatly affect repulping. Optimized laboratory repulping conditions for papers A–F are summarized in **Table V**. The papers can be repulped to a high degree using the two-pH repulping process with reasonable processing conditions, times, and temperatures. These papers were also repulped by the alkaline repulping process under similar processing conditions (oxidant level, time, temperature, and shear), and the repulping results were significantly lower than those by the two-pH repulping process (**Table VI**).

Dry strength response from recycled fiber

The dry tensile strength of 4-g laboratory handsheets made from repulped paper B using the two-pH repulping process was weaker than the virgin B laboratory handsheets made from diluted stock taken before the blend chest (**Table VII**). These results are expected, since recycled fibers characteristically have decreased fiber network strength from changes in fiber morphology (fiber length, apparent density, etc.) and a reduced bonding area from the effects of repeated drying *(18)*.

Although the percent repulped was about the same for each oxidant, the loss in dry strength for the recycled paper may depend on the standard redox potential of the oxidant during repulping *(19, 20)*. Using the repulping conditions in Table VII for paper B, the observed oxidation strength was $Na_2S_4O_8 > KHSO_5 > H_2O_2$. (Standard electrode potentials, E^0, should be measured during repulping to confirm the order.) The strongest oxidizing agent, $Na_2S_4O_8$, may be reacting to a greater extent with paper fibers at this oxidant level (10% on dry paper) compared to the other oxidants and thus greatly reducing the dry tensile strength of the repulped paper. However, significantly lower levels of strong oxidant (i.e., less than 3%) are not expected to drastically affect the strength of paper made from recycled fibers *(2)*.

Field trials

The two-pH repulping process was directly compared to the alkaline repulping process at different paper mills on papers C and E. The results are summarized in **Table VIII**. The equipment used to repulp paper C was a high-shear/low-consistency hydropulper with a rotor on the bottom of the vessel. The equipment used to repulp paper E had twin side-mixing

Paper	Reagent	Percent reagent on paper	Percent rewetter on paper	Process temp., °C	Process time, min	Shear at 3000 rpm, min	Percent repulped
A	$KHSO_5$	5.0	0.1	70	120	3	58
D	$Na_2S_4O_8$	2.5	-	70	60	3	56
E	$Na_2S_4O_8$	3.0	0.1	85	120	6	77
F	$KHSO_5$	3.0	0.1	90	240	6	25
F	$KHSO_5$	3.0	0.1	90	240	9	64

VI. Alkaline repulping process. The paper was repulped at pH 11.

Reagent	Process pH	Percent repulped	Dry tensile, kPa
Virgin paper	-	-	4685
$Na_2S_4O_8$	4/11	82	1703
$KHSO_5$	4/11	88	2828
H_2O_2	4/11	87	4057

VII. Dry strength response of paper B laboratory handsheets from furnishes repulped in the laboratory by the two-pH repulping process. (The paper was repulped for 1 h at 70°C using different oxidants at 10% on paper.) Virgin laboratory handsheets were made from diluted stock (B) taken before the blend chest, and dried and cured under the same conditions as the repulped handsheets.

Percent PAE in paper	Percent oxidant on paper	Process pH	Process time, h	Percent repulped
		Mill 1 (Paper C)		
1.0	3% $KHSO_5$	3/11	3	93
1.0	3% $KHSO_5$	11	12	<50
		Mill 2 (Paper E)		
1.0	3% $KHSO_5$	3/11	5	95
1.0	3% $Na_2S_4O_8$	11	12	<50

VIII. Field Trials. Process temperature was 70–85°C. The paper consistencies were 4–6%. Two-pH process: 0.1% rewetter on paper; the paper was processed at the lower pH for 2 h before increasing the pH with NaOH. Alkaline process: The paper was processed at pH 11.

blades that did not apply much shear to the paper mixture, and a longer processing time was needed to repulp the paper. In both mill trials, the alkaline repulping process was unable to repulp the paper, whereas the two-pH repulping process readily defibered the paper.

SUMMARY

Repulping unbleached and bleached paper containing high levels of permanent wet-strength resins, in particular polyaminoamide-epichlorohydrin (PAE) resins, can be readily accomplished by using a two-pH repulping process. The process is more effective with a rewetting surfactant that decreases the time to wet the paper, enabling the oxidant to penetrate the paper so that uniform oxidation of the substrate can occur. The ease and effectiveness of the process were shown in the laboratory and at two paper mills that were having great difficulty in repulping their unbleached paper by alkaline processes. **TJ**

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