Recycling of Wet Strength Paper

Tandon* Rita, Mathur* R.M., Kulkarni A.G.**

ABSTRACT

Secondary fiber is going to be one of the major fiber resources for the paper industry in the years to come. It is estimated that waste paper will meet 50 percent of the increased demand for raw materials by year 2000 and it has already become an internationally traded commodity. In India, majority of the paper mills are utilizing waste paper as raw material and a substantial amount of waste paper is being imported from different countries. Wet strength paper used for packaging of liquids and cement products is one of the several varieties of imported paper which unlike other grades of waste paper poses problems in slushing operations in the conventional hydrapulpers, due to presence of wet strength resins. Studies conducted at CPPRI have revealed that chemistry plays a vital role in imparting wet strength to the paper due to which specific repulping conditions are required to achieve higher yield with low energy consumption. An appropriate combination of chemical and mechanical treatment facilitates the repulping operation keeping the energy demand low and maximizing the yield. The paper highlights the various aspects influencing the repulping efficiency of wet strength papers and the role of chemical additives on resin depolymerization. Although the findings are at laboratory scale but are expected to be translated successfully at mill scale.

INTRODUCTION

The growing demand for paper, paperboard & newsprint in our country through the next millennium and the need for massive capacity expansion to the tune of 8.0 million tons, require a strong and sustainable raw material base. With the limitations of forest produce and also the size constraints with agro based mills, the use of recycled fiber (RCF) perhaps will be acceptable to the industry by virtue of well developed processing techniques.

Today majority of paper mills (63.4%) are using waste paper as raw material and account for 31% of total paper production in the country. Around 35% of recovered paper is being imported from countries like U.S. which has been continuously rising with the increasing demand. The apparent reason for high imports is low recovery rate, which is around 17% at present and the deteriorating quality of indigenously recovered paper. This situation is hardly going to improve unless an organized domestic collection system is adopted in the country. Under the circumstances the use of imported paper is inevitable to keep the product quality.

**Central Pulp and Paper Research Institute,
P.O. Box No. 174,
Saharanpur - 247 001 (U.P.)**

In our country, most of the production from waste paper is confined to packaging grades, and long fibered imported waste paper is used as top liner or bottom liner in the production of duplex board for quality reasons. The quality of RCF from imported waste is superior than our virgin fiber but lot of problem are faced during processing due to the presence of contaminants. Among the different varieties of imported waste paper, wet strength paper used for liquid packaging and for cement products is one, which unlike other grades of waste paper poses problems during slushing due to presence of wet strength resins resulting in high reject content, low yields and high electrical energy consumption.

The wet strength paper keeps its integrity because of its chemistry. This chemistry also defends it in the pulper unless it is attacked with the right combinations of chemical and mechanical energy. The wet strength resin in paper forms a cross-linked insoluble, covalently bond net work of organic polymer and hemicelluloses, between and/or around the fiber contact. Depending on the chemistry of resin, the network may become insolublised by resin-resin crosslinking and or by crosslinking of cellulose or hemicellulose through resin molecule (1).

Urea formaldehyde (UF) and polyaminoamide epichlorohydrin (PAE) are the two most commonly used wet strength resins, Urea formaldehyde has been declining over the past several years since it requires acidic pH during curing and PAE is the predominant resin used today (83%) as it requires neutral/alkaline pH during curing, preferable for neutral/alkaline sizing.

Detailed studies conducted on repulping of wet strength paper has revealed that paper containing permanent resin usually requires drastic conditions for repulping and a combination of chemical and mechanical treatment is more effective than mechanical treatment alone with little cost added due to chemical, however the added benefits are low power consumption, increased productivity, efficient contaminant removal,

TABLE -1

CLASSIFICATION OF WET STRENGTH RESIN

Resin Class	Wet Strength	Typical pH During Papermaking	Type Of Curing	Percent Usage (Global)	Repulping Condition
Urea Formaldehyde (Aminoplast)	Permanent Low Cost	3.8-4.5	Acidic	1.0	Acidic
Melamine-Formaldehyde (Aminoplast)	Permanent Low Cost	4.0-5.5	Acidic	1.0	Acidic
Aminopolyamide - epichlorohydrin (PAE)	Permanent	5.0-9.0	Neutral/ Alkaline	83.0	Strong Alkaline Oxidative
Polyamine-epichlorohydrin	Permanent	5.0-9.0	Neutral/ Alkaline	8.0	Strong Alkaline Oxidative
Aldehyde Polymer					
-Polyacrylamide glyoxal	Temporary	4.5-7.5 (Neutral)	Neutral	5.0	Mild Alkaline
-Dialdehyde starch	Temporary	4.5-6.5 (Acidic)	Acidic		Acidic

TABLE -2

PHYSICO-CHEMICAL CHARACTERSTICS OF DIFFERENT WET STRENGTH PAPER/BOARD (IMPORTED PRE-CONSUMER WASTE)

Sample	Extract pH	Ash % w/w	Alcohol/ Benzene Extract w/w	Dry Strength NM/gm.	% Wet Strength Wet/Dry 100	Possible Resin Type	Proposed Repulping Conditions
KCB - 1 (Unbleached)	6.9	6 - 8	2.76	*ND	Poor wetting	Permanent	Highly alkaline
Sack kraft (Unbleached)	6.5	0.87	3.08	77.5	23.0 (After16hrs.)	Permanent	Highly alkaline
Bleached-1	7.2	14.0	1.4	*ND	Poor wetting	Permanent	Oxidant With alkali
Bleached-II	7.5	4 - 19		59.4	15.0 (After 2hrs.)	Temporary	Mild alkali

● N.D. not determined due to improper sample size.

low rejects, improved quality of fibers and improved strength properties. The present paper discusses the various aspects of efective repulping of wet strength paper, with respect to optimum process conditions, effect of process variables and impact of pulper configuration on repulping efficiency.

RESULT AND DISCUSSION

Behaviorally, wet strength resins can be classified as

- Temporary resin - 70 - 80% wet strength is lost after 2hrs soaking.
- Permanent resin - >20% wet strength is lost after 2hrs soaking.

But chemically, resins can be classified into three board classes as given in Table -1 The different resin type has typical pH range for best working and this pH range on the finished paper gives an idea of probable resin type.

IDENTIFICATION OF RESIN TYPE

Following tests have been found very effective in identifying the resin type on the paper, which subsequently facilitated in formulating the treatment method for repulping

Test-I

Determination of wet Strength as percentage Of dry strength (Tappi Method T 456-OS-68) - Differentiates temporary and permanent resin

Test - II

Extract pH - Differentiates acid curing and neutral/alkaline curing resin

Test-III

Solvent extraction (A'ch/Benz.) - Quantifies resin content

The above tests were performed for four varieties of imported wet strength paper containing both bleached and unbleached varieties and based on the test results, the samples were subjected to specific treatment methods. The result are depicted in Table -2.

Three varieties - Sack Kraft, KCB and

Bleached-I belonged to permanent resin class and bleached - II contained temporary resin. Extract pH clearly shows that all the varieties contained neutral/ alkaline curing resin and hence the possible resin type is PAE which is the most predominant type. Based on the findings the samples were subjected to alkaline repulping conditions using NaOH as chemical, however in case of bleached variety oxidants were used in combination of NaOH to prevent yellowing caused by NaOH alone.

OPTIMIZATION OF REPULPING CONDITIONS

To arrive at optimum repulping condition for different varieties, the samples were treated at specified temperature and pH with reagents in a closed vessel with gentle mixing to augment the performance of the reagents used in the process. After treatment the paper mixture was subjected to high shear rate in a laboratory disintegrator for 6 minutes and accept yield after passing the stock through a vibratory slotted

TABLE -3
OPTIMIZATION OF PROCESS CONDITION FOR DIFFERENT VARIETIES OF WASTE PAPER

Variety	Chemical Used	Chemical Concentration g/l	Pulping Time hrs.	pH	Temperature ^0C	Shearing Time in min. at 3000 rpm	Accept Yield %
Sack Kraft	-	-	0.0	7-7.5	70	6	4.0
	-	-	0.0	7-7.5	70	20	46.0
	-	-	3.0	7-7.5	120	6	48.2
	NaOH	0.6	0.25	9.5	70	6	22.5
	NaOH	0.6	0.25	9.5	70	20	84.3
	NaOH	1.2	2.0	>11.0	120	6	60.3
	NaOH	2.5	1.5	>11.0	120	6	71.0
	NaOH	5.0	1.5	>11.0	120	6	83.0
	NaOH	5.0	0.5	>11.0	120	10	88.6
	NaOH	7.5	1.0	>11.0	120	6	87.0
	NaOH	7.5	1.0	>11.0	120	10	94.0
*K.C.B							
Sample-1	-	-	-	-	70	6	42.6
	NaOH	1.0	1.0	>11.0	70	6	85.2
	NaOH	1.6	0.5	>11.0	120	6	87.0
	NaOH	2.0	1.0	>11.0	70	6	88.4
	NaOH	2.0	0.5	>11.0	120	6	87.5
Sample-2	NaOH	0.4	1.0	9.5	70	6	75.0
	NaOH	0.6	1.0	10.5	70	6	84.0
	NaOH	1.2	1.0	11.0	120	6	75.6
*Bld. -1.	-	-	-	-	70	6	53.0
	$Ca(OCl)_2$	0.6	1.0	8-9	70	6	75.0
	$Ca(Ocl)_2$	0.6	1.0	6-7.5	70	6	80.2
	H_2O_2	0.1	1.0	7/11	70	6	65.0
	H_2O_2	0.2	1.0	7/11	70	6	78.0

a - Kraft Corrugated Board
b - Bleached Variety of Paper
c- Theoretical Yield on ash basis
Sack Kraft = 98%
KCB - 93%
Bld. - 86%

d- Accept yield % - Defibered stock obtained after passing the pulper stock through Serle Vibratory screen with 0.2 mm slots opening screen with 0.2 mm opening was taken as a measure for repulping efficiency. Sodium hydroxide was used as a repulping aid for unbleached variety. Although traditionally hypochlorite is being used to break down PAE resins during pulping (1), however being environmentally unfriendly the shift is towards use of chlorine free chemicals. Potassium Monopersulphate has been found to be the most effective chemical for repulping of wet strength paper (2) but it is economically unviable under Indian conditions being an imported chemical. For our studies $H^2 O^2$ has been used as an alternate to hypo for bleached variety.

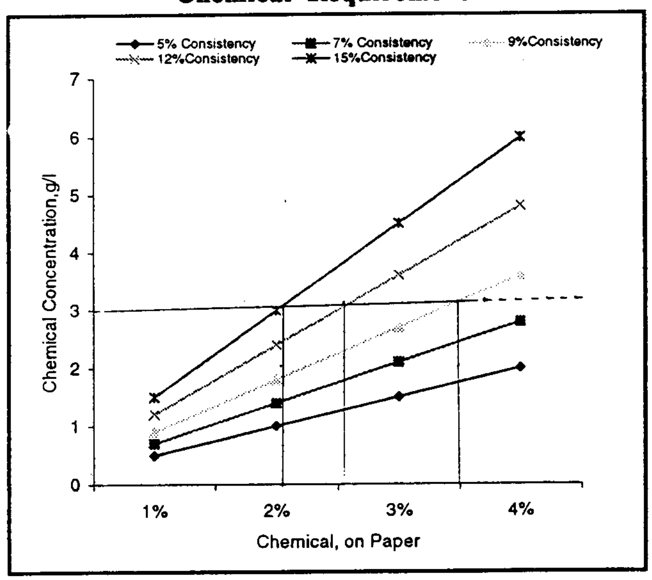
Table-3 summarises the optimum repulping conditions for all the three varities of wet strength paper. since bleached -II variety contained temporary resin, a mild alkaline condtions using 0.1% $Na_2 CO_2$ during slushing was suficient to get an yield close to theoretical value. The results at a glance clearly indicates that sack kraft requires more drastic conditions for repulping. The yield is best at high pH, high temperature and high shear rate, presumably due to high amount of resin in it. To achieve an yield close to theoretical vale i.e. 98% an optimum chemical concentration of 5-6 g/l, a pH level>11.0 and pressurized cooking at 120 °C for 30 minutes followed by disintegration in hydrapulper is required. However for the mills which do not have digester facilities, slushing in the hydrapulper at 80-90 °C using Na OH can be done, but a minimum slushing time of 60 minutes will be required. It was observed that mechanical treatment alone is not sufficient to defibrise the sack paper and requires specific process conditions for repulping. For KCB variety, however an optimum chemical concentration in the range of 1.0-1.5 g/l at 70 °C during slushing with minimum pulping time of 30 minutes will be sufficient to get an yield of 88% as against 42.6% under same repulping conditions but without chemical aid. For the bleached - I variety a selective two pH range i.e. 7/11 at 70 °C has been found to be the most suitable condition using $H_2 O_2$ as an oxidant. A minimum of 1 hour rection time is required which includes 30 minutes for $H_2 O_2$ to react under neutral conditions followed by NaOH under alkaline conditions. In all these experiments, it is observed addition of chemical aid accelerates the rewetting phenomena in these varieties, eventually facilitating the fiber to fiber friction during slushing operation.

FACTORS INFLUENCING REPULPING EFFICIENCY

i) Pulper Cofiguration:

To repulp wet strength paper, the right chemistry combined with mechanical energy are required for optimal results. Mills with repulping equipments that has both high agitation and shear are best suited for increased efficiency. Mills equipped with high-density pulper are more benefitted due to low energy and chemical consumption. Further with batch operations, control of process variables is easier. Additionally it is beneficial to have repulpers linked to steam lines since desired temperature will increase the efficiency. Mills having low consistency pulper will require a secondary pulper or defibrator for achieving best results.

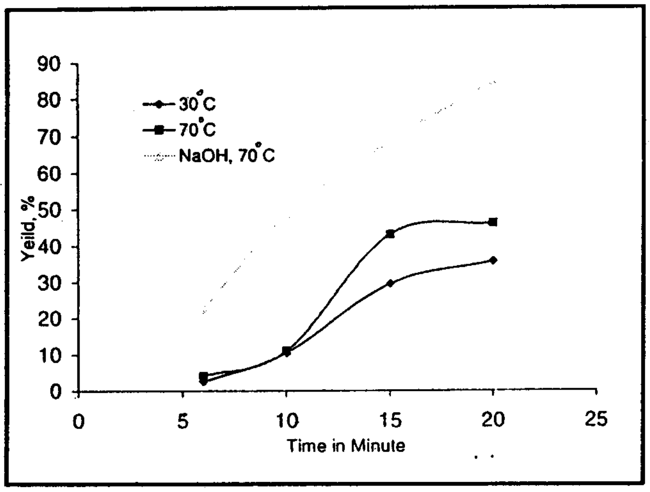
Fig.-1 Effect of Consistency on Actual Chemical Requirement



ii) Process variables

The important process variables affecting the repulping efficiency are pH, Temperature, Consistency, time and Shear rate. Besides high shear rate., pH emperature and consistency have been found to have profound influence on repulping efficiency. Highly alkaline pH is more effective for unbleached grades containing PAE type resin while for bleached variety repulping at selective two -pH range is more favorable. Moderate to high temperature positively influences the efficiency. Repulping at high consistency would reduce the pulping time, chemical requirement as well energy requirement. Effect of consistency on actual chemical requirement is shown in Fig 1. At same level of chemical charge in percent on paper, the concentration will be low at lower consistency and hence for desired chemical concentration an additional dose will be required thus increasing the cost. By reducing the consistency from 15% to 5% the cost will increase by 3.0 times.

Fig. - 2 (a) Effect of Process Variables on Repulping Efficiency of sack Kraft Paper



The influence of different process variables on repulping efficiency are depicted in Fig. 2 (a-c). pH has a very distinct role on repulping efficiency. Acid curing resin would require acidic pH for repulping while neutral/alkaline curing resin would require neutral to alkaline pH for repulping depending upon the amount of resin on the paper.

A higher temperature more than 60 °C is required for repulping of wet strength paper as the high temperature facilitates the penetration of chemical into the paper. A minimum retention time of 30 minutes is essential for reaction to take place between resin and chemical aids.

ROLE OF REPULPING AIDS ON RESIN DEPOLYMERISATION

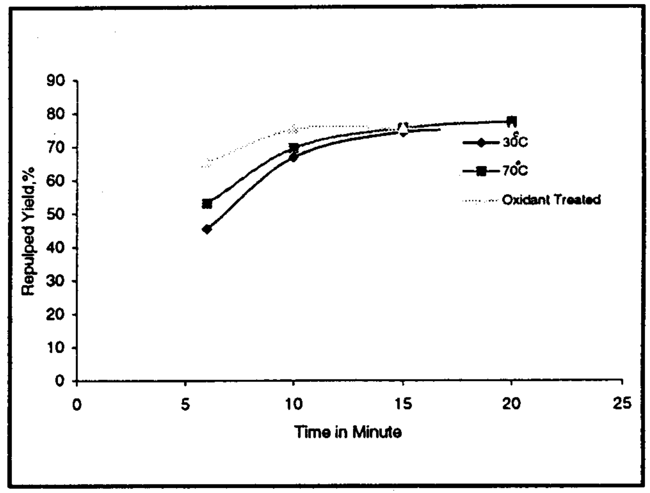
Each chemical added has a specific role on repulping chemistry.

Sodium Hydroxide: In unbleached grades treatment with strong alkali (pH above 11) at 70 °C may work by saponifying the ester cross links between resin and hemicelluloses and is more effective in the range of 60-80 °C.

Calcium Hypochlorite: At pH 6-7 the HOCI attacks the cross-link itself or the polymer chain at the cross link site to form secondary amine and an aldehyde. At higher pH the predominant free amine groups are attacked by OCI anion (1)

Hydrogen Peroxide: The secondary amine and tertiary amines are susceptible to oxidation, which predominates at low pH when strong oxidant is used.

Fig. - 2 (b) Effect of Process Variables on Repulping of Bleached Variety of Waste Paper



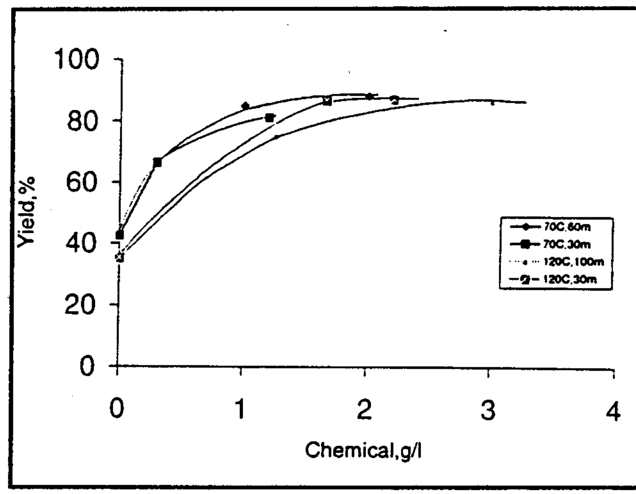


Fig. - 2 (c) Effect of Process Variables on Repulping Efficiency on K.C.B. Variety

With the use of strong oxidant two pH process is more preferable to single pH process (3).

FIBER CLASSIFICATION AND PHYSICAL STRENGTH PROPERTIES

The fiber classification clearly reveals that the quality of fiber is much better than Indian virgin fiber as shown in Table -4. The + 20 fraction is as much as 80% in sack kraft and is close to soft wood pulp. The unbleached fiber can be further upgraded with bleaching to be used in the production of fine grades, while the bleached variety can be used directly for writing printing grades.

There has been a drastic improvement in physical strength properties with chemical addition. The burst factor is improved by 40% and breaking length by 28% with NaOH in unbleached grades.

TABLE - 4

FIBER CLASSIFICATION OF RECYCLED PULP STOCK USING BAUER MCNETT CLASSIFIER AND COMPARED WITH BLEACHED PULPS FROM OTHER FIBROUS RAW MATERIAL

Type of Pulp	Retained on 20 mesh	Retained on 50 mesh	Retained on 100 mesh	Passing Through 100 mesh
	values in (%)			
Sack Kraft	80.4	9.2	5.8	4.6
KCB	68.0	17.0	4.0	11.0
Bleached Variety	48.9	24.7	9.7	16.7
Rice Straw[4]	2.7	18	25.3	54.0
Bamboo[4]	43.8	3.6	16.5	36.1
Hard Wood[4]	0.9	27.1	52.2	19.8
Soft wood[4]	82.5	6.5	5.0	6.0

CONCLUSIONS

- Wet strength paper known to be hard to-slush variety can be successfully repulped by proper understanding of chemistry of wet strength resins. An appropriate combination of chemical and mechanical treatment is necessary to obtain high fiber yield with low energy requirements.
- Pulper configuration plays a vital role in slushing the wet strength papers, High consistency facilitates improved fiber to fiber friction maintaining high chemical concentration, both of which are necessary for high repulping efficiency.
- Other process variables of vital importance are pH, temperature and shear rate maintained in the pulpers. Proper control of these process variables is essential for improved efficiency.
- The fiber classification indicates that the fiber quality of sack kraft is close to softwood pulp, which can be used for production of cultural variety by further upgradation through bleaching. Pulps obtained from bleached variety of wet strength paper can be used directly for production of writing/printing grade paper.

EXPERIMENTAL

Single pH-Process

Commercial paper was cut into 1" x 1" pieces and diluted to a weight ratio of 2% before heating to desired reaction temperature. Chemicals are added while gently stirring the paper. In case of using oxidants pH was maintained using NaOH. The paper was mixed for minimum 60 minutes reaction temperture and then transferred to lab disintegrator (Tappi Test Method T 205 om -88) and sheared for 6 minutes at 3000 rpm. Yield was determined by passing the defibred stock through a vibratory slotted screen having 0.2 mm opening and the rejects were dried at 105 °C.

Two pH-Process

In two -pH process the oxidant was added and mixing continued for 30 minutes at reaction temperature. The pH was adjusted to about 11 with aqueous Na OH and mixed for another 30 minutes at reaction temperature. The mixture is then transferred to disintegrator and sheared as mentioned above.

The pulp obtained were subjected to Bauer Mc Nett classification and evaluated for physical strength properties.

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