

Wet strength papers

MUKHERJEE A.K.*, BARAR P.**,
CHAKRABORTY K.L.**, SOOD A C.** and
SARKAR M.C.**

INTRODUCTION

For many practical uses the water and moisture sensitivity of ordinary paper proves to be an unsurmountable obstacle. Water leaf paper shows excellent dry strength properties, but almost all of this strength is lost when the paper is wetted by water because dry strength is due primarily to hydrogen bonding (and probably some ionic bonding) and these bonds are destroyed by water, which is very effective at forming hydrogen bonds itself. Therefore, development of wet strength requires the formation of different types of bonds which are not adversely affected by exposure to water. The earliest method for developing wet strength was to fuse the cellulose fibers to one another, either by heating the paper to very high temp. or by partially solubilizing the paper with 75% sulfuric acid. The latter is the method by which parchment paper is produced. The first chemical method for improving wet strength involved the use of formaldehyde which can form methylene bridges between hydroxyl groups on the surface of cellulose fibers.

Wet strength is usually reported in terms of the ratio of wet tensile to dry tensile strength, expressed as a percentage. Paper possessing a wet tensile strength greater than 15% of dry tensile are considered to be wet-strength papers.

The most important wet-strength agents are applied by beater or wet end addition; i.e., they are added to the pulp before the sheet is formed at the "wet-end" of the machine. Aluminium sulfate is often added to cure resin or to retain anionic Urea-formaldehyde resins. Additives that are not substantantive to (absorbed by) paper fibers must be added to the paper after sheet formation. This procedure is usually less cumbersome than addition to the paper stock.

Saturation of paper with water reduces its strength to about 3-10% of its dry strength. Animal glue decreases the rate of absorption of water: if the paper is treated with both formaldehyde and animal glue it will have true wet strength. Treatment with 75% sulfuric acid produces "vegetable parchment," which has high wet strength, but the treatment seriously changes other sheet properties. By means of modern commercial resins, wet-strength of 20-50% of dry strength can be obtained. Addition of 1% resin can cause a three to six fold increase in wet strength.

B. USES OF WET STRENGTH PAPERS

Wet strength papers are widely used for packing purpose. for making multi-wall paper sacks, paper bags and wrapping papers and containers employed for protection of flowers and moist or frozen food, such as fish vegetable and ice-creams, towels, paper handkerchief and toilet tissues. Wet strength paper is now frequently used for horticultural labels, currency notes, laundry tags, maps, blue prints, posters and other articles subject to out of-doors exposure.

C. TYPE OF RESIN

1. Urea-Formaldehyde
2. Melamine-Formaldehyde
3. Polyamine and Polyamide
4. Glyoxal
5. Dialdehyde starch
6. Chitosan
7. Miscellaneous
8. Newer Resin

*Department of Textile Technology
Indian Institute of Technology
New Delhi - 110 016.

**Nuchem Plastice Limited, 20/6, Mathura Road,
Faridabad-121 006.

be added to the stock to ensure maximum retention of resin in the paper. The acidity of the stock should also be adjusted to pH 4-5 by adding alum and hydrochloric acid. The quantity of resin should not be more than 3-4% of the dry weight of fiber. 60-70% of the resin added to the aqueous pulp suspension is normally retained on the fiber.

Urea-formaldehyde resins generally react less rapidly than melamine-formaldehyde resins which are, in general, lower than epichlorhydrine-amine resins. The use of a rapidly curing resin permits the mill to sell the paper as soon as it is manufactured, without storage and warehousing. However, repulping of "broke" (trimmings and rejected papers produced in the mill) is more difficult if wet-strength resin cures too rapidly. A cationic U-F resin requires ten to fourteen days to develop full cure (at 20°C) whereas the anionic resin requires about twice as long. Paper containing U-F resin can be repulped.

Urea formaldehyde resins do not show great resistance to hydrolysis. At a pH of 4-6, these resins can be hydrolyzed fairly readily, but they resist hydrolysis at pH 8-10. It has been reported, however, that under favourable conditions, paper treated with U-F resins will retain its full wet-strength for six to eight years.

CHARACTERISTICS

Low viscosity liquid Solid content $68 \pm 2(\%)$
or
Powder
Shelf life (20°C) :
 Liquid : 3-6 months
 Powder : 1 year
Pot life (20°C)
 0-48 hr.
Usual room temp. Setting time . 3-10 hr.
Hardener 5-10% Starch to give wet resistance.

DISADVANTAGES

1. Slow cure
2. Cationic resin coated—10-14 days full cure
Anionic resin coated—21-28 days full cure
3. Hydrolyses readily at pH 4-6

ADVANTAGES

1. Cheap
2. Repulping possible
3. Retains property (wet strength) 6-8 years.

USE :— Urea resin adhesive mixed with starch is used in making water resistant and high humidity resistant paper board boxes and corrugated paper board used in packing industries. Generally starch and dextrin pastes are used but these are not water resistant. Urea resin and hardner to the extent of 5 to 10% (dry wet) on the weight/starch depending on the degree of water resistance dsired and nature of the starch is used.

C.2 MELAMINE FORMALDEHYDE RESIN

The melamine resins colloid are the first materials to be successfully applied to paper by introduction at the wet end of the paper making process.

The characteristics of a typical melamine colloid is as under :

Form-White, Free flowing Powder

Reactive resin content	: 100%
Solid Content	: 93%
Nitrogen Content	: 38.9%
Shelf life	: 12 months (See Fig. 1-3)

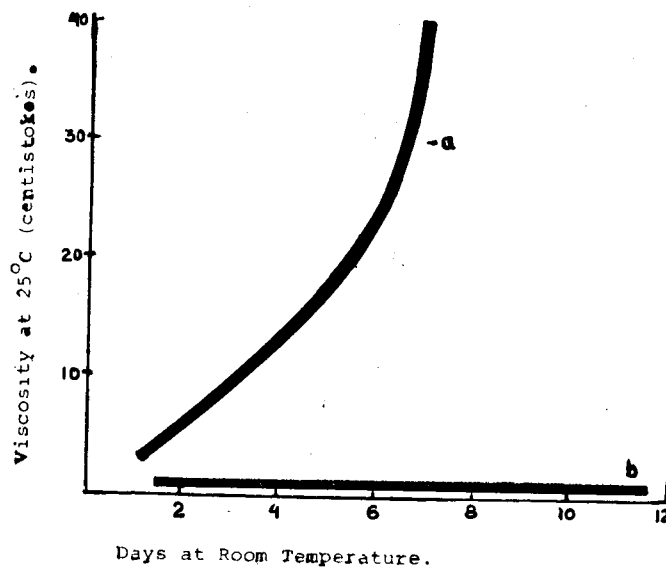


Fig. 1. Stability of Melamine Acid Colloid Solution on storage ; a-12% Normal, b-6% Normal

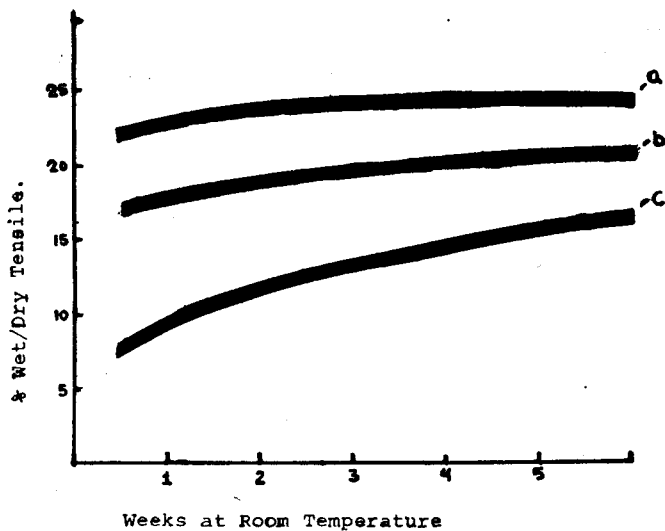


Fig. 2. Development of Wet strength by using Melamine Acid Colloid Solution (solid resin addition 1.5%) in treated Bleached Sulphate (Canadian Freeness-424 ml) Pulp after Storing at Room Temperature at various pH ; a-pH 4.5 b-pH 5.5, C-pH 6.5.

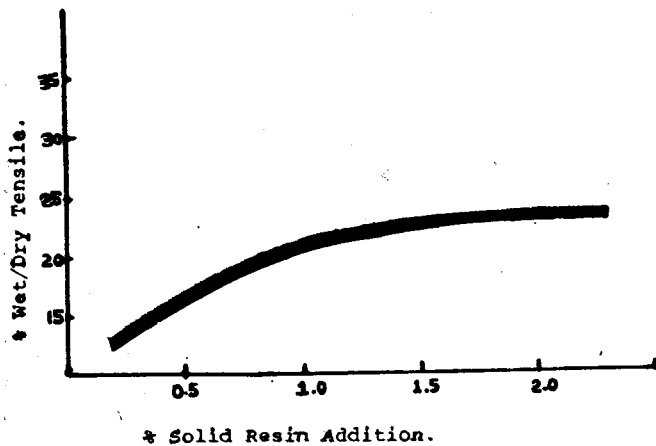


Fig. 3. Effect of % Resin Addition by using Melamine Normal Acid Colloid Solution on Full cure Wet strength of Bleached Sulphate Pulp (Canadian Freeness-425 ml).

Melamine acid colloid solution is made as follows :

8.4 ml. of concentrated Hydrochloric Acid is added to 184 ml. of water heated to 35-38°C. The acid solution is vigorously agitated; and 25 g of a spray-dried melamine formaldehyde powder resin (Molar ratio 1:3 M.f) as above is added. When dissolution is complete the solution is allowed to stand for 3 hours for the colloid to develop. The solid content of this

colloidal solution is about 12%. It remains stable at least 3 days, but then rapidly increases in viscosity and gels. After dilution of the solution further to 6% solid, where the life will be indefinitely higher is to be added to a suitable point between the beaters and the head box. The quantity of resin will usually not exceed 3% solids on dry fibre.

Cationic Acid Colloid solution has a direct affinity for cellulose pulps which normally carry a negative charge and the use of alum to assist retention is, therefore, unnecessary. The acidity of the stock may require adjustment however, and alum, hydrochloric acid or sodium carbonate may be used for this purpose according to circumstances. Optimum wet strength is obtained if the acidity of the stock is adjusted so that the pH of the paper as it leaves the machine is within the range of 4.5—5.0.

Between 70 and 85% of the resin added is retained in the paper web after formation and cures fairly rapidly on passing over the drying cylinders. A further improvement in wet strength usually occurs during storage if the paper is reeled hot.

TABLE-I

COMPARISON OF U-f & M-f

PARAMETER	U-f	M-f
Rate of cure	Moderate	Fast
PH tolerance	Low	High
Nature of pulp	Selective	Any kind
Resistance to hydrolysis	Poor	Good
Beating period	More	Less
Effect of humidity	Dimensional Change	No change
Sticking to Yankee Drier	—	Low
Gluing problem	None	None
Resistance to delamination	Good	Excellent
Folding endurance	Good	Excellent
Dry strength	Increase	More increase
stain resistance	Poor	Good
Abrasion resistance	Poor	Good
Heat resistance	Poor	Good
Curing conditions	147-163°C in 3 min.	130-190°C in 1.5 min.

TABLE—II
APPLICATION OF AMINO RESINS BY BEATER ADDITION

Resin 3% weight	Bleached sulphite pulp				Un-bleached Kraft pulp			
	Without alum		With alum		Without alum		With alum	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
	Tensile	strength	(1b/in)		Tensile	strength	(1 b/in)	
None	5.4	1.2	5.3	1.2	11.0	1.2	10.2	1.2
U—f	6.8	1.7	9.0	3.3	15.8	3.6	20.5	8.2
Anionic U—f	10.0	5.3	10.0	5.3	21.4	7.5	21.0	9.1
Cationic M—f Acid Colloid	9.4	4.1	10.0	4.4	18.0	5.5	19.4	6.6

APPLICATIONS OF M.F. RESINS

M.F. resins are used for making superior grade wet strength paper where ever U f coating is not suitable. One of the major application of M.f. is to make decorative laminates. The various steps in making decorative laminates are given below :

1. Assemble 6—8 layers (core) of P-f bonded kraft paper.
2. Put a M—f impregnated alpha-cellulose paper.
3. Put the decorative layer (0.008-0.010") :
Alpha-cellulose paper + 40-50% U.f. or M.f. resin.
4. Put protective overlay (0.001-0.003") : Highly refined alpha-cellulose pulp + 65—75% M.f. resin.
5. Cure under heat and pressure.

DISADVANTAGES OF AMINOS

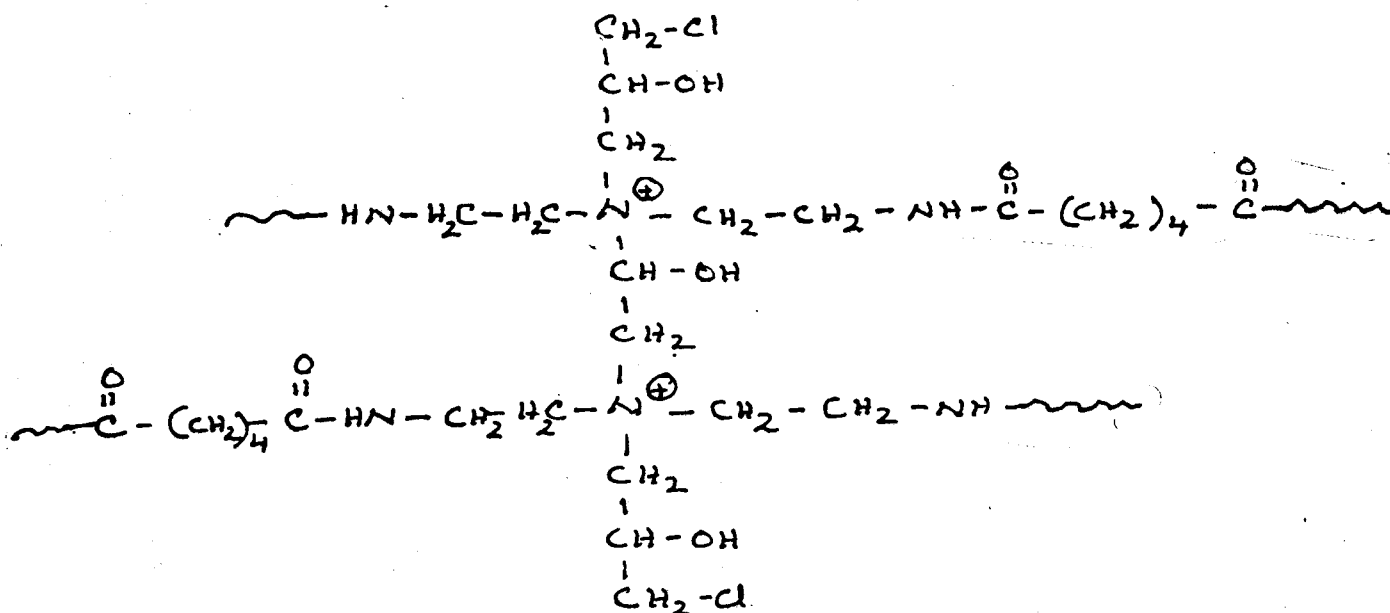
1. Acidic pH (around-4.5) during curing
2. Deterioration of paper :
Embrittlement
Reduction in Absorbancy
Harsh Hand.
Resins hydrolyze at low pH
4. Gradual wet-strength reduction during storage.

C.3. POLYIMINE AND POLYAMIDE WET—STRENGTH RESINS

The amino-formaldehyde resins have the disadvantage of requiring acid condition for curing. The recommended pH of around 4.5 causes embrittlement and deterioration of paper, reduces absorbancy and develops a harsh hand. These characteristics are especially undesirable in tissues and towelling. In addition, the wet-strength resins are hydrolyzed at low pH resulting in a gradual reduction of wet strength on storage, especially when the paper is wet. It was apparent that a wet strength agent which would cure at pH 7 or higher was desired.

In 1952, Daniel and Landes patented a polymer of polyalkylene polyamine and epichlorohydrin as a wet strength resin which could be cured at pH levels as high as 10. Several years later, a polyamide-polyamine epichlorohydrin product was introduced to paper mills, and this type of resin has found general acceptance as a wet-strength agent for absorbent papers and other grade made at pH around 7. The resin is produced from an aliphatic dicarboxylic acid, such as, adipic acid, an alkylenepolyamine, such as, diethylene triamine, and epichlorohydrin. The product is an efficient wet strength resin which cures at pH higher than that required for the formaldehyde resins.

A typical polyamide resin produced from adipic acid, diethylenetriamine, and epichlorohydrin would have the structure :



Loss of hydrogen chloride is accelerated under basic conditions, and the resulting epoxide group is free to react with cellulose or other amino group.

The polyamide resins, like other wet-strength resins may be introduced to paper stock at any convenient location after the major refining work is done and before the sheet is formed, as for example, at the fan pump. The resins are retained efficiently, and absorption occurs rapidly. The resin may be added at any pH from 4 to 10, although the range 6-8 is usually prepared.

There are several significant difference between polyamide resins and the amino-formaldehyde resins. The polyamide resins cure over a broad pH range, and the rate of cure is affected to a lesser extent by change in pH. At the recommended pH conditions amino-formaldehyde resins reduce the absorbancy of paper. but the polyamide resins have little effect. At low levels of add-on, the polyamide resins are more efficient than the amino-formaldehyde resins, but higher ultimate wet strength can usually be obtained using urea-or melamine formaldehyde. The polyamide resins are well retained without the use of aluminium sulfate although addition of 25 ppm sulfate ion is reported to help in achieving maximum efficiency at high levels of addition.

Paper containing U-f and M-f wet strength agent is usually repulped with acid, whereas that containing polyamide resins require hydrochlorite or a high pH. The amino-resin increases the dry strength more than do the polyamide resin.

Amino Polyamide-epichlorohydrin resins are significantly more expensive than formaldehyde based resin but the higher cost is offset by other advantages mostly the advantage of making paper at neutral to alkaline pH. These include properties, such as, improved softness and absorbancy, no tendency towards embrittlement on aging, and reduced paper machine corrosion. Another important advantage is the elimination of formaldehyde usage.

CHARACTERISTICS

1. Gel time (200 g)	: 2-4 hr.
Viscosity	: 120 NS/m ³ at 21°C
Shelf life	: 6 months, 20°C
Curing pH	: Higher than Aminos

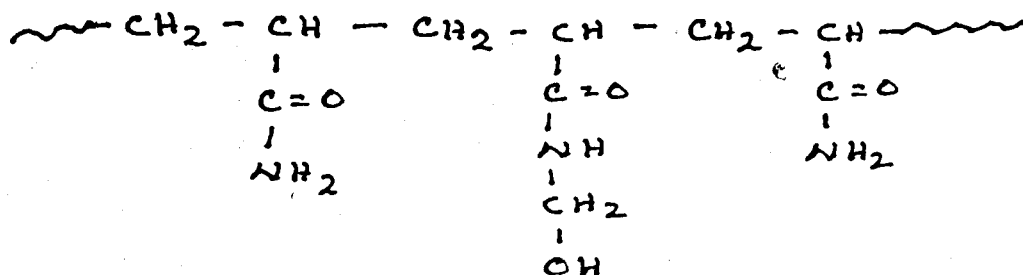
TABLE—III

COMPARISON WITH AMINOS

PARAMETERS	AMINO	PA
pH range	Acidic	4—10
Rate of cure (effect of pH)	Great	No significant
Paper Absorbancy	Reduction	No effect
Wet-strength (at comparable add on)	High	Higher
Alum	Necessary	Not necessary
Repulping conditions	Normal	Special
Dry strength	Increase	More increase
Softness	Less	More
Aging	Brittle	No change
Machine corrosion	High	Low
Cost	Low	High

C.4. GLYOXAL RESINS

Another class of wet strength resin is based on the reaction product of polyacrylamide and glyoxal. This resin can react with hydroxyl groups on cellulose fibers through the glyoxal functionality to form hemiacetal bonds, resulting in improvements in paper wet strength although, not to same extent as amino-polyamide-epichlorohydrin resins. The base polyacrylamide usually contain a small amount of cationic co-monomer, such as, dimethyldiallyl ammonium chloride to make the resin substantive to pulp fibers.

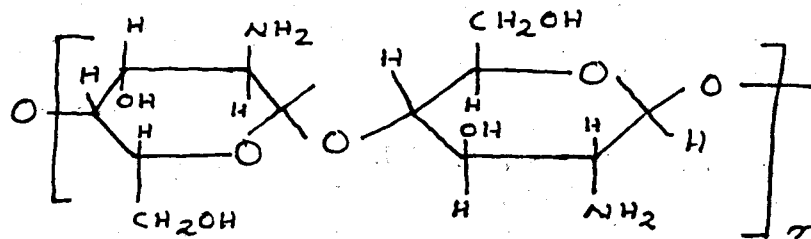


C.5. DIALDEHYDE STARCH

Dialdehyde starch, made by periodic oxidation of cornstarch, is the newest type of resin to achieve commercial attention as a wet strength resin. Dialdehyde starch is anionic in nature and can be used as wet and additive only if the paper fibers have been treated with cationic starch or synthetic cationic retention acids. High amounts of aluminium sulfate are required for retention of dialdehyde starch. Dialdehyde starch produces only a temporary wet strength, but cationic dialdehyde starch confers more permanent wet strength. Temporary wet strength is useful in towels and sanitary tissues where wet strength is required for only a few seconds and where permanent wet strength can cause clogging of plumbing and septic tanks. In addition to temporary wet strength can dialdehyde starch offers extremely easy broke recovery high wet strength without loss in absorptivity, rapid development of wet strength, and excellent improvement in dry strength properties. It is the only paper additive that imparts significant improvement in wet and dry strength without causing broke recovery problem.

C.6 CHITOSAN

Chitosan (Poly 2-aminodeoxy-1,4 glucoside) is not a single substance, but a group of partially deacetylated products of various degree of polymerisation. Chitosan is insoluble in water, concentrated alkalise, alcohol, and acetone, but dissolves readily in dilute acid. It has also been shown to impart wet strength to paper. The polymer, although potentially available in large quantities from shell-fish wastes has never become a commercial significant product.



C. 7 MISCELLANEOUS

In addition to the urea-formaldehyde, melamine-formaldehyde, and dialdehyde-starch resins, other resins may impart some wet strength, but are used primarily for purposes other than wet strength.

Small amount of neoprene latex added at the wet end of the paper making machine gives high wet strength and resistance to a variety of chemicals. Saturation on paper with styrene-butadiene, acrylic or butadieneacrylonitrile latex for use in manufacturing book covers, making tape and gaskets confers wet strength and other properties to paper. Latexes also change many other properties of paper, e.g., hand (the feel of the paper), elongation, stiffness, dimensional stability, edge and internal tearing resistance folding endurance and tensile strength. Therefore, they are not used when wet strength improvement is the only change desired.

Because latex particles are not readily retained by pulp; their use is frequently more troublesome, but aluminium sulfate aids their retention. Saturation with phenolic resin, like saturation with latex, produces a resin filled sheet that has high wet strength. However, the treatment of paper with latex of phenolic resin changes its properties in such a fundamental way that it is not usually called "wet-strength treatment".

C. 8 NEWER RESINS

Polyethylenimine was used in Germany during world War-II as a wet strength agent. It has never become commercially significant, however, it confers several unique properties. It retards the rate of beating of pulp and should be added after the pulp is beaten. Wet strength develops as the pulp is dried, and water absorbancy is not affected.

Cereal xanthates, produced from cereal starches or flours produces permanent wet strength and increase dry tensile strength and folding resistance.

Polyacrolein gives paper with high, permanent wet strength and good dimensional stability. The polyacrolein must be treated with sulfur dioxide or a sulphite to make it water.

D. MECHANISM OF WET STRENGTH FORMATION

With the exception of polymeric amines, all effective wet-strength resins undergo crosslinking reaction and react with functionality present on the surface of cellulose pulp fibers. Two mechanisms for wet strength development have been proposed.

The protection theory suggests that the resin form a crosslinked network around existing - fiber bond and prevents swelling and disruption of these bonds.

The new bond theory proposes that the wet strength resin creates new fiber-fiber bonds that are covalent and thus are not broken on exposure to water. The protection theory is supported by the fact that a given concentration of aminopolyamide-epichlorohydrin resin imparts wet strength that is a relatively constant percentage of dry strength in various pulp furnishers, even though the absolute values of wet and dry strength might vary substantially.

The new bond-theory is supported by the fact that wet and dry strength are increased by approximately the same increment with either formaldehyde-based or aminopolyamide-epichlorohydrin wet-strength resins.

E. REPULPING

Repulping of paper is necessary for two reasons. During paper manufacture broke (waste) is produced either during breaks on the paper machine or as trim

produced during the rewinding process. For the paper making process to be economical, this must be recycled. Also, the use of waste-paper furnishes is increasing as the cost of virgin-pulp furnishes increase.

Paper containing wet-strength resins is more difficult to repulp than not-wet-strength paper. Therefore, the repulpability properties of wet strength resins must be considered when choosing a resin. U-f and M-f resins can be readily repulped under acid conditions. Alum is used in the repulping operation when these resins are used. Paper containing polyamide-epichlorohydrin resins are not readily repulped under either acidic or basic condition. Oxidising agents, such as, sodium hypochlorite are usually required for repluping in such cases. Presumbaly, the oxidant attacks the polyamide backbone and breaks down the resin. Paper contain ing poly (methyl diallyamine) epichlorohydrin wet-strength resin is very difficult to repulp. The hydro-

carbon backbone of this resin is not subject to attack by reagents commonly used in aqueous systems.

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