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THESIS: Wet Strength Resins

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for: Dr. Ellsworth Shriver

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ABSTRACT:

Wet strength is defined as a paper which has extraordinary resistance to rupture or disintegration when saturated with water. This definition has been interpreted as if a paper sample retains more than 15% of its dry strength when wetted, it can be considered to have wet strength properties.

Wet strength resins are chemicals that aid in wet strength, and they have been around since the 1940's. These wet strength resins help to protect paper and paper products from breaking down in the presence of water and high humidity. There are many uses for wet strength resins these days. Some of these are: To protect from outdoor weather, to aid in drying and wiping, to wrap up food products, and to help in things that must be totally submerged in water.

The resins compared are urea formaldehyde, melamine formaldehyde, polyamide epichlorohydrin, and polyamine epichlorohydrin. These resins when compared showed that the newer PAE resins had better wet strength properties than the older formaldehydes. Because of this reason and that formaldehyde is a public hazard and is regulated by OSHA, the PAE resins came out better in cost and overall usage.

INTRODUCTION:

The strength property of paper is contributed mainly by fiber - fiber bonds. When paper is wetted in water, the swelling of fibers weakens these bonds and paper loses a substantial amount of its strength. When a paper is saturated with water and it contains extraordinary resistance to rupture and disintegration. This definition has been interpreted that if a paper sample retains more than 15% of its dry strength when wetted, then the paper is considered to have wet strength properties.

Wet strength resins were first developed in the 1940's in order to protect paper and paper products from breaking down in the presence of water and high humidity. The first resin to be invented was the urea formaldehyde resin, followed by the melamine formaldehyde resin and then many others. Many uses have come about because the uses of paper and paper products have expanded and the likelihood of being exposed to water have increased as well. Some examples of various uses that wet strength in paper would be useful for are:

1. Protection from outdoor weather.

Examples: Building blueprints, outdoor posters, packing cases, and paper bags.

2. Aid in drying and wiping products.

Examples: Paper towels, napkins, wiping tissue, and dusting media.

3. Wrapping for food products.

Examples: Paper bags, meat wrapping, frozen food wrapping, and prepared food wrapping.

4. Aid for products totally submerged in water.

Example: Filter paper, tea bags, and photographic paper.

The chemistry for these resins are different for each of the resins. So I will discuss a few of the more popular resins individually. These resins are urea formaldehyde, melamine formaldehyde, polyamine and polyamide epichlorohydrin.

First of the resins is urea formaldehyde. The chemistry of this resin involve two stages in the production of it. The first stage involves nucleophilic addition of a nitrogen containing compound called methylation. Also in this stage the amide group from urea is involved (App. 1, Fig 1). The second stage involves condensation polymerization between the methanol compound, promoted by high temperature and low pH of about 4.5, to give methylene or ether linkages, with the elimination of the water molecule in each linkage in the polymerization process (App. 1, Fig 2). The urea formaldehyde resin belongs to the acid curing resins group, and chemically, this means that the condensation reaction which results in polymerization of the resin to the water - insoluble stage is initiated by hydrogen ions, which must be supplied by an acidic material. This material can be alum or a mineral acid, such as sulfuric acid or hydrochloric acid. The pH of the paper machine using the urea formaldehyde resin must be below a pH of 5 and preferably a pH of 4 - 4.5. A typical cationic UF resin attain about half of its wet strength off the machine and the remaining wet strength property will be obtained after about 2 to 3 weeks of natural aging.

Melamine formaldehyde can be produced by two different methods. The first method, which is considered the most important method commercially, and uses calcium cyanamid (App. 1, Fig 3). The second method of production involves urea (App. 1, Fig 4). The melamine reacts with the formaldehyde at slightly alkaline conditions of pH 7-8, to form a series of methylol melamines. Depending on the number of moles of formaldehyde present, a range of products from monomethylol to hexamethylol melamine can be formed. The melamine formaldehyde resins are

of high molecular weight and are made by condensing polymerization of two or more monomer units with the elimination of water under high temperature and low pH. It is at this low pH (about 2) that a number of cations co-react to form a still larger positively charged particle. About 20 of these monomer units will condense to form melamine formaldehyde colloids. It has been found that a 3 to 1 molar ratio of formaldehyde to melamine seems to give the best melamine formaldehyde colloids as wet strength resins. The wet strength which is obtained from the use of melamine formaldehyde is more durable than that which is obtained from urea formaldehyde. This can be attributed to the greater amount of functional groups present in the melamine formaldehyde resin.

The polyamide and polyamine epichlorohydrin resins are made by reacting polyamine or an amine containing polymer with epichlorohydrin in water. The epichlorohydrin alkylates and crosslinks the polyamine to a moderate molecular weight. In other words, the epichlorohydrin reacts with the secondary amine groups and transforms them to secondary and tertiary groups. Thus, a cationic resin is obtained with reactive groups which promote crosslinking. The crosslinking is then arrested by dilution or by reducing the pH to convert amine groups to their acid salts, by acidifying the aqueous resin solution (App. 1, Fig 5). Whether the reaction partner of epichlorohydrin is a polyamide, a polyamine, or an amine polymer, its amine groups may be primary, secondary, or tertiary. These act with epichlorohydrin by different results (App. 1, Fig 6). The most important PAE resins are derived from secondary aminopolyamides. The PAE resin has a reel wet strength of about 50 % and obtains full wet strength properties after about 3 weeks. Also these resins do not require acidic conditions to react. Thus, the PAE resins have become the most commercially important thermosetting product for the production of wet strength paper.

The wet strength resins have become a very important part of the paper making industry, and without them paper would be back in the stone ages. It seems that the progresses that have been made have shown that the formaldehyde's are now almost inferior to the newer alkaline resins. This is also true because of the public pressure from the hazards of the formaldehyde.

PROCEDURES:

To compare the different resins, handsheets were made and tested by the following procedures.

- * First a 50/50 handsheet softwood blend was made comparing of 180 grams of each in the refiner with 23 liters of water.
- * Then the blend was refined for about 45 minutes until 500 freeness was reached, with 20 pounds of load attached.
- * A consistency check was then run, which came to about 2%.
- * Then each of the resins were measured out at 5, 10, 15, and 20% of the O. D. fiber and added in the dicinigrator of the Noble and Wood handsheet maker.
 - A) The Urea was first heated to about 200 F on a hot plate before addition.
 - B) The melamine had to be made a little acidic before it would react.
- * After about a 15 minute wait for the resins to react with the pulp slurry, the measured slurry samples were dumped in the settling tank which contained a screen at the bottom of it.
- * Then the water was drained out of the settling tank, leaving a fiber mat on the screen.
- * Next the screen was pressed in a felt between two rollers to remove more of the water.
- * The screen with the fiber mat was then rotated on the dryer drum to dry the fiber mat (paper).
- * After drying the paper, it was then removed from the screen and put through the dryer one more time.
- * The sheet was then weighed and placed in a conditioned room for about a week and a half.

- * After conditioning, the paper samples were cut into 15mm strips in which half were left dry and half were completely wetted.
- * Then all the samples were tested on the tensile machine for tensile strength.
- * Finally the results were compiled and analyzed and will be discussed in the next sections.

RESULTS:

	Dry Load	Wet Load
	<u>(KGF)</u>	<u>(KGF)</u>
0%	1.804	.027
5% Melamine	2.134	.322
10% Melamine	2.357	.331
15% Melamine	2.086	.426
20% Melamine	2.016	.476
5% Urea	1.984	.302
10% Urea	2.156	.319
15% Urea	2.026	.403
20% Urea	1.960	.435
5% Amide	3.346	.649
10% Amide	3.737	.758
15% Amide	3.152	.765
20% Amide	2.987	.781
5% Amine	2.821	.803
10% Amine	3.906	.878
15% Amine	3.265	.926
20% Amine	2.773	.983

Urea + Melamine cost about \$1.85/ lb, and PAE resins cost about 2.45/ lb.

DISCUSSION:

In this section my results will be discussed.

First of all, the wet strength of paper seemed to increase as the percent of resin added increased, for each of the resins compared (App. II). Also the newer PAE resins seemed to give a considerable amount more of wet strength than the urea and melamine formaldehydes. This seems to be almost two times as much (App. II). This trend occurred because the formaldehyde resins need a higher percentage of resin to O.D. fiber to get the same bond strength in water as the PAE resins.

Second the dry strength of the paper as the percent resin increases seemed to rise until 10% and then steadily decrease. This, I thought was because the extra resin bonds helped in the voids in-between the fibers that were already bonded (App. III). Then when more resin was added, the resin took over some of the fiber- fiber bonds, giving a weaker bond, and causing the dry strength of the paper to decrease. Also, as occurred before in the wet strength, the PAE resins seemed to have a larger dry strength than the urea and melamine formaldehydes for each of the different percent of the added resins.

Finally, the wet strength as compared to the dry strength at 10% where the dry strength is at its maximum, showed that the urea and melamine formaldehydes obtained about a 15% wet strength to dry strength value. While the PAE resins obtained about a 22% wet strength to dry strength value (App. IV). At 20%, the wet strength to the dry strength in the polyamine was about 35%, and in the polyamide about 27%, and in the urea and melamine formaldehydes was about 24% (App. V). But because the PAE resins have much higher dry strength, their wet strength percent is a much higher value than the formaldehydes.

CONCLUSIONS:

- * The polyamide and polyamine had superior tensile strength values versus the UF and MF resins.
- * The cost of the polyamide and polyamine per pound were a better buy than the UF and MF resins. Because you need about two times as much formaldehyde resin as PAE resin, and the costs were (FORMALDEHYDE= \$1.85/ lb, PAE= \$2.45). As you can see the PAE resins are not twice as much, so that is why they are the better buy.
- * The PAE resins were easier to use and control because of their pH flexibility.
- * UF and MF resins are used less than the PAE resins because the formaldehyde contained in the resins are a public concern and are controlled by OSHA.
- * All in all the new resins were superior by far in my study!!!

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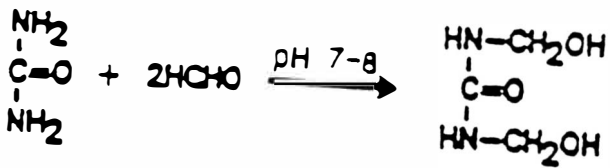
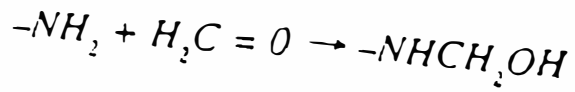
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App I

Fig I



Reaction of urea with formaldehyde.

Fig II

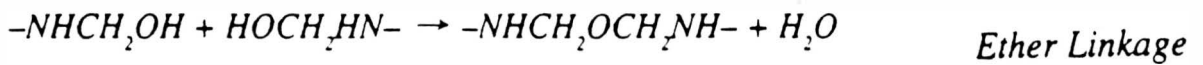
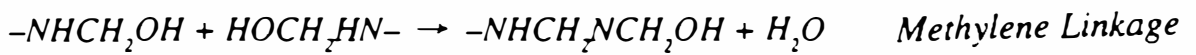
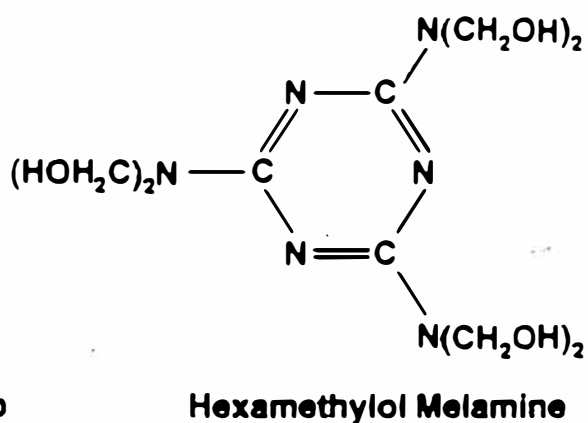
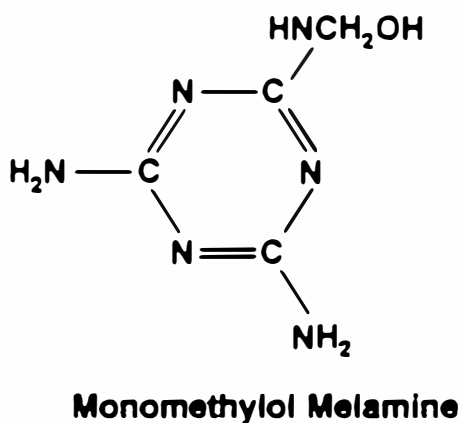
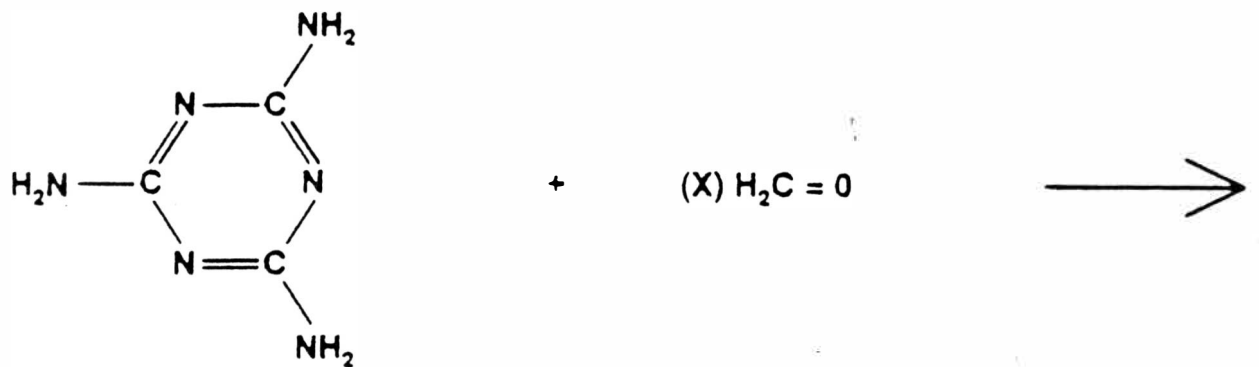


Fig IV cont.



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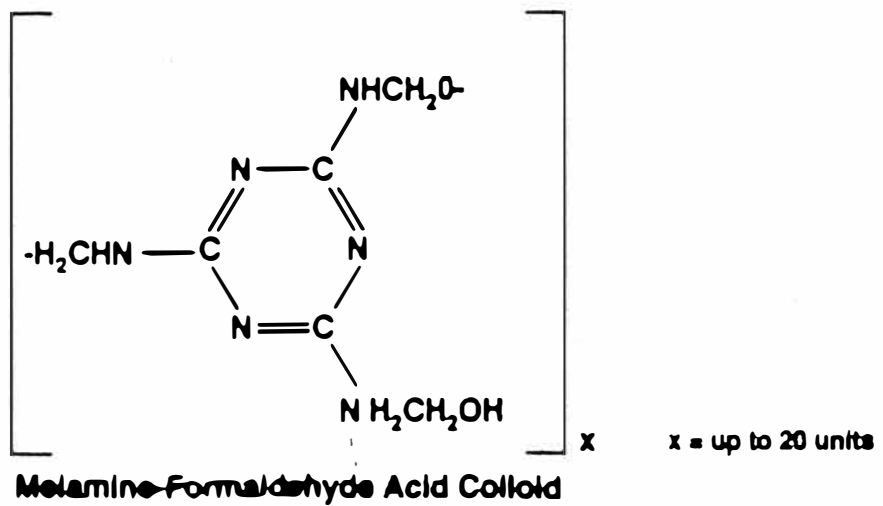
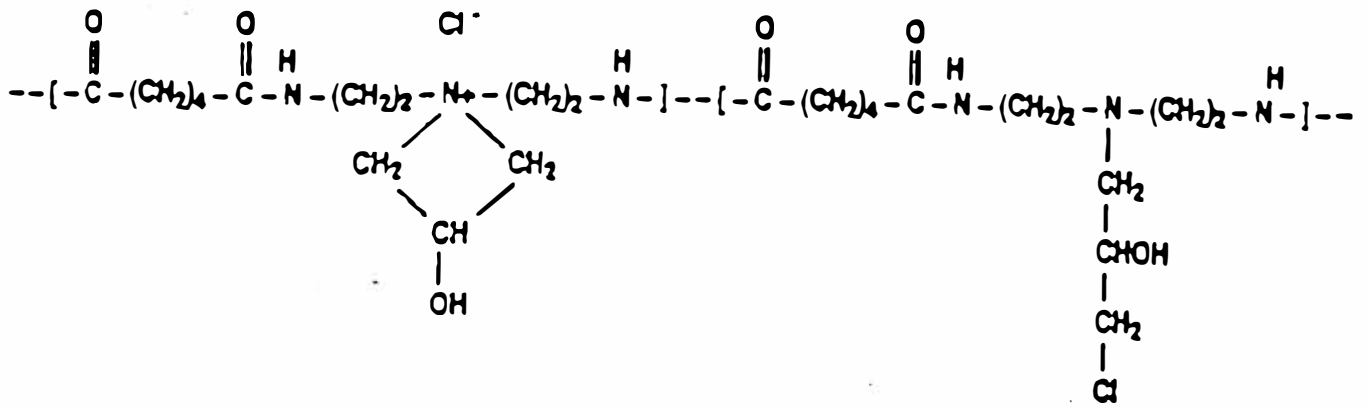


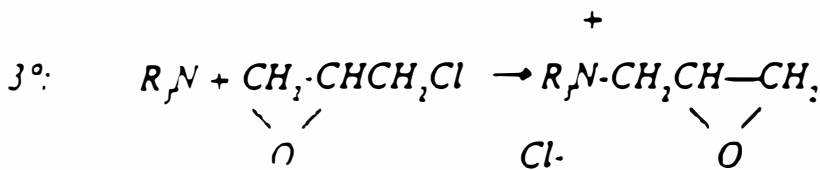
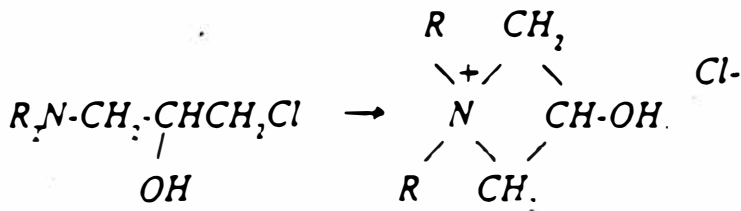
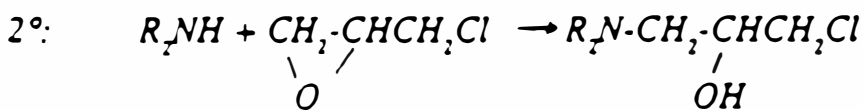
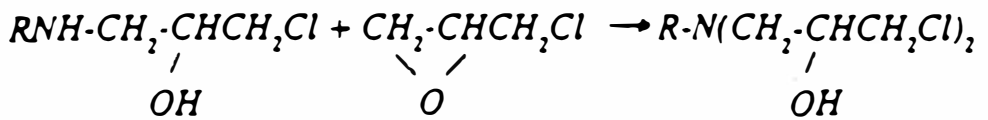
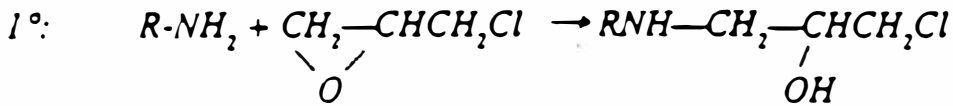
Fig V



Azetidinium structure

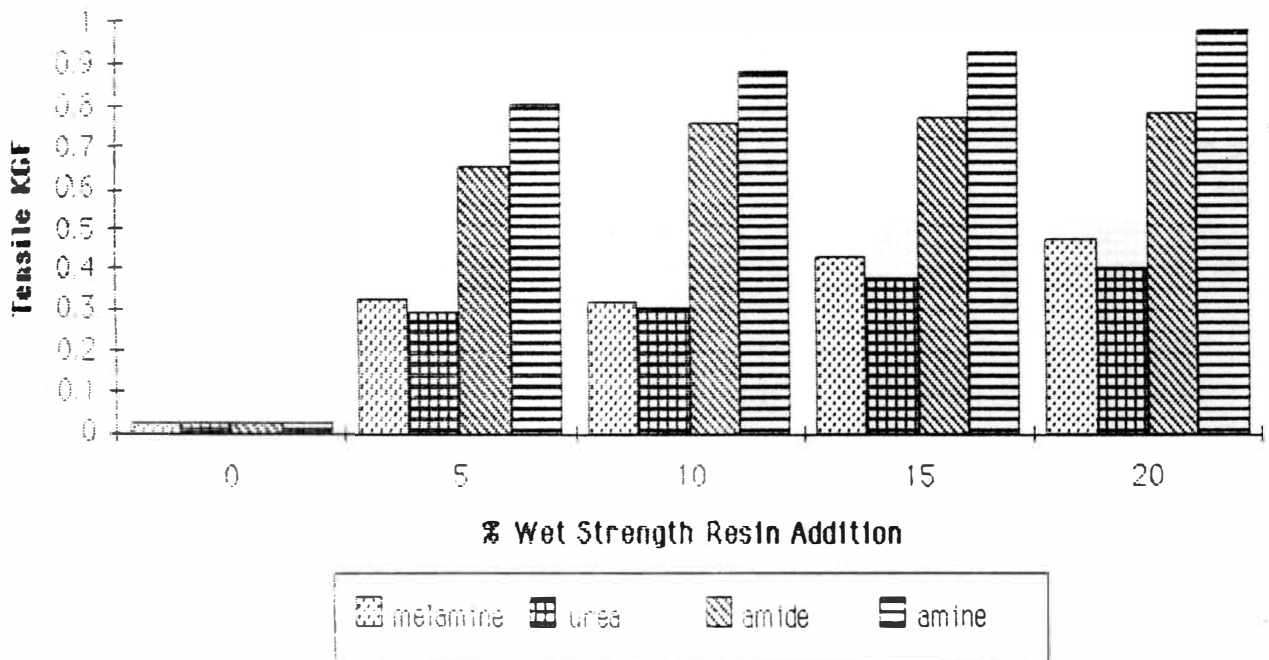
Chlorohydrin structure

Fig VI



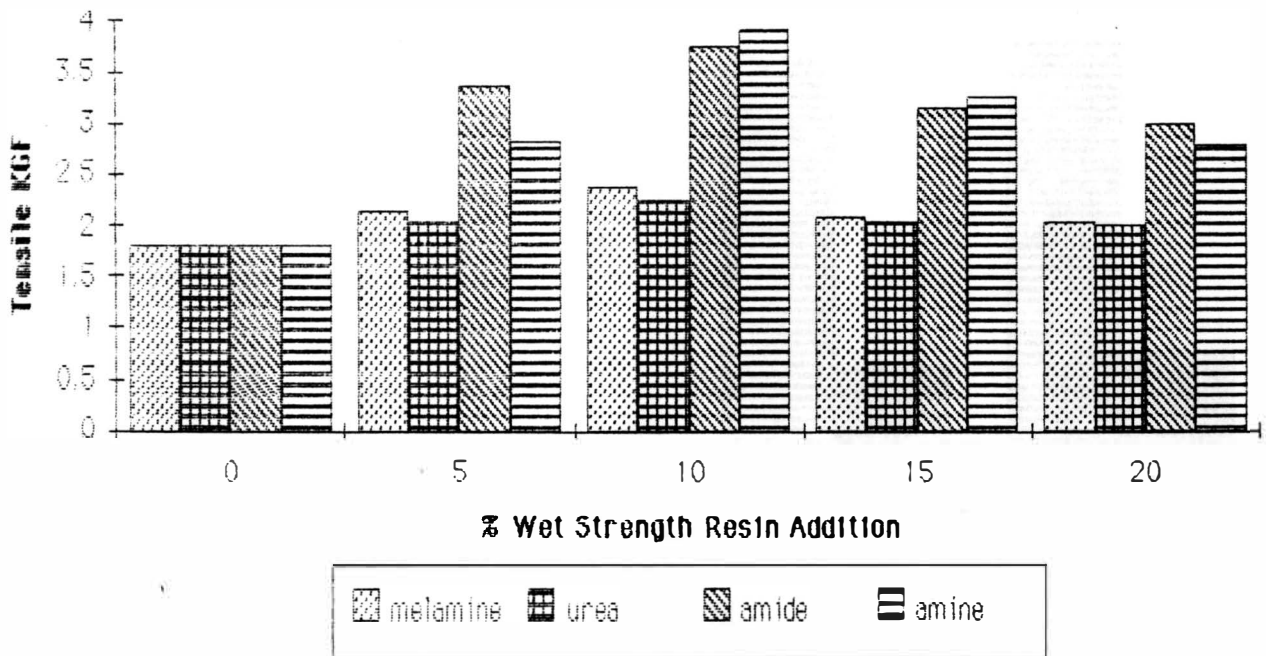
APP II

Wet Strength of Handsheets with % Wet Strength Addition



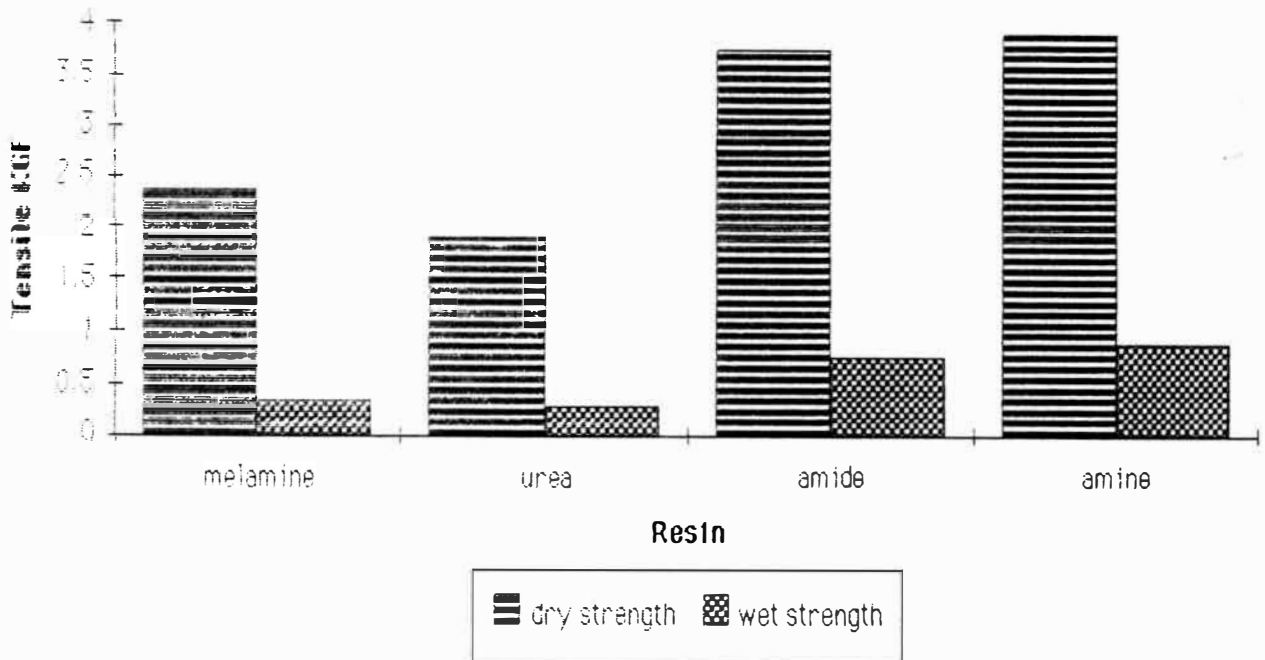
App III

Dry Strength of Handsheets with % Wet Strength Addition



App IV

Dry Strength vs. Wet Strength at 10% Addition



App. V

Dry Strength vs. Wet Strength at 20% Addition

