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The Influence of Urea & Melamine Formaldehyde Resins upon Absorbency, Softness, & Dry Strength Characteristics of Paper

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THE INFLUENCE OF UREA & MELAMINE FORMALDEHYDE RESINS UPON ABSORBENCY, SOFTNESS, & DRY STRENGTH CHARACTERISTICS OF PAPER.

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ABSTRACT

The literature is reviewed on urea and melamine formaldehyde resins and their possible effects upon softness, absorbency, and physical characteristics. The standard tests of these sheet properties are also defined and reviewed. Experimental work is described in which resin treated sheets were prepared and evaluated. The resultant data is evaluated from the standpoint of property variations and is graphically illustrated. Conclusions are drawn as to the feasibility of resin treatment for soft absorbent sheets.

INTRODUCTION

One of the most significant factors in the expansion of the paper industry, has been the ever increasing multitude of uses to which paper has been put. Such a product, must, in its diversified uses, come into contact with water or moisture either by exposure to the atmosphere or by virtue of its utility.

Ordinary paper will inherently lose a great deal of its strength characteristics when wetted to any degree, and eventually disintegrate upon prolonged exposure. Obviously for some papers to perform their function efficiently, an ability to withstand attack by water is of paramount importance. To meet this demand, numerous processing methods have been developed over a period of years whereby papers of high strength in the wet state might be produced. This development centered about the discovery that incorporation of small amounts of a synthetic resin followed by polymerization could confer wet strength upon a sheet. The reaction of these small quantities of resin in producing the wet strength property and the economy of operations involved afforded the basis for widespread and large scale production.

Britt(1) traces three distinct phases in the development of synthetic resins, particularly urea-formaldehyde and melamine-formaldehyde.

The first of these phases, occuring in the period 1938-1942, was the use of water soluble urea-formaldehyde condensation products of a low degree of polymerization as a tub size or surface application. This method achieved good wet strength but neccessitated treatment of the sheet after formation on the paper machine.

The next phase, emphasized by Landes (2) eliminated after-treatment by application of a melamine-formaldehyde resin which could be added directly to the paper machine stock, and which would be absorbed by the fiber. This

resin was highly polymerized but still water soluble, and most important, possessed an inherent affinity for fiber by virtue of being a cationic colloid. Contemporary urea-formaldehyde resins did not have this inherent affinity for fiber but could be precipitated upon the fiber by means of alum.

The third and most recent phase has been the development of a cationic urea-formaldehyde which is affinitive to fiber, and extremely versatile under a variety of operating conditions. This versitility has been immeasurably increased by modified urea-formaldehyde resins which permit high degrees of condensation without loss of water solubility.

Since wet and dry are only relative, it is natural that the wet strength of paper should have an effect on its dry strength characteristics. Such is actually the case. Resins are increasingly being utilized primarily for their beneficial influence upon dry strength.

High wet strength is to no avail if it destroys other properties upon which the use of paper is dependent. A facial tissue with wet strength is visualized as being a valuable product; but obviously it is usless unless softness and absorbancy are retained. This is a typical problem in the incorporation of wet strength and is of particular interest to this report.

UREA-FORMALDEHYDE

Urea-formaldehyde resins as well as melamine-formaldehyde resins may be devided into two groups: anionic and cationic (2). In turn each group may be classified as low condensed, orapproaching monomeric proportions, and highly condensed or polymeric. Both anionic and cationic resins are available in modified forms (3).

Stock suspensions possess a negative charge (4), and, therefore, anionic urea-formaldehyde must utilize alum as a mordanting agent to provide effective retention upon the fiber. The behavior of anionic urea-formaldehyde resin (Uformite 467) is described by Myers and Morin (5). These authors have showed how good performance with these resins cannot be obtained unless a three way interaction among the fibers, alum, and resin takes place.

Sigvardt (4) points out that bleached pulps are more strongly anionic because of the presence of carboxyl groups associated with the cellulose. In conjunction, Gruntfest (6) found that difficulties in applying anionic urea-formaldehyde resins to bleached pulp can be overcome only with careful control; but at times it is neccessary to use cationic varities of resin.

Cationic urea-formaldehyde is "tailor made" for versitality and ease of operation. By reason of its attractive charge to pulp, the delicacy of the problem of controlling operating conditions is eliminated along with the use of alum. However, care must be exercised that the very same cationic property that can aid retention does not hinder it (6). This can happen if the pulp is only slightly anionic and the resin strongly cationic, so that the charge of the pulp may be reversed. With urea resins the charge density can be controlled so that this situation may be avoided.

Versatility of the urea-formaldehyde resins, either anionic or cationic, is enhanced by coreacting other reagents into the polymer molecule (modified resins). When sodium bisulphite is used as the coreactant, a resin of extreme hydrophilic character is synthesized (7). This permits retention of the water solubility of the resin at higher degrees of condensation than would otherwise be possible.

The desireability of each of the various types of urea-formaldehyde in conjunction with their effects on absorbency and softness, will be examined in a following discussion on these characteristics.

MELAMINE-FORMALDEHYDE

Maxwell and Landes (8) describe a typical melamine-formaldehyde resin (Parez 607) as being positively charged, and easily attracted to cellulose fibers. In addition, the resin is equally effective on any form of cellulose fiber, although the results are more noticeable when used with a strong pulp. The presence of alum is not required to obtain good resin retention and wet strength.

Melamine-formaldehyde resin is prepared (9) for use by adding one pound to a gallon of dilute hydrochloric acid in the proportion of one mole of the resin to 0.8 mole of the acid; the concentration of hydrochloric acid in the total colloidal solution is approximately 1.5%. The corrosiveness of such a solution constitutes a problem, and for permanent installations, stainless steel and Saran tubing are recommended.

An important consideration is the reuse of the broke; melamine-formaldehyde treated papers should be reused as quickly as possible. Since melamine-formaldehyde treated papers cure and retain wet strength longer than urea-formaldehyde treated papers, they are more difficult to defiber.

SOFTNESS

"Softness may be defined (10) as one of several properties of a sheet of paper. In the case of tissues and toweling softness is often used to indicate a combination of surface smoothness with stiffness e.g., the sheet may be crumpled in the hand to yield a sensory estimate of softness. Thus,

estimated, softness is related to surface smoothness and lumpiness or lack of stiffness and thickness of the sheet. In several restrictive uses of the term, softness is apparently related to stiffness alone."

Softness is evaluated by the Clark softness tester as prescribed by TAPPI 451 m-45.

One source (11) commenting on the value of Clark softness values, notes fair correlation between the instrumental and subjective estimates of softness (as determined by crumpling by hand). Note is also made of the inconvenience and possible error of the instrument.

One source (12) reports the need of a common unit of softness, enabling industry to standardize softening ingredients.

McPherson (13) brings to notice the confusion which has arisen because of the lack of a means of adequate instrumental evaluation of softness.

Auten (14) attributes softness to the ease with which strain relieving fiber dislocations can take place when the sheet is bent. This is borne out by the lubricative nature of effective softening agents, such as glycerine, ethylene glycol, and oils (12, 13).

At normal concentrations (2-3%), the quantitative effect of urea-formaldehyde and melamine-formaldehyde resins upon the softness of a sheet, is not directly stated in any sources that the author could discover.

Myers (15) finds that harshness and lack of flexibility results at higher concentrations of resin and suggests the use of softening agents. One manufacturer (16) offers a "paper softering oil" which it is claimed will offset any stiffness or hardness resulting from high resin content.

Gruntfest and Young (3) relate softness to the degree of polymerization of the resin used. Contrasting polymeric resin to monomeric resin, they find that the former is an inter-fibre precipitation, while the latter is

intra-fibre. The conclusion is that the resin outside the fibre interferes with their movement relative to one another, and therefore stiffens the sheet to a much greater extent than resin inside the fibre. The existence of intra-fibre precipitation is confirmed by the staining behavior of treated fibres, particularly in the case of urea-formaldehyde resins.

The softest papers are made from highly bleached pulps (16), and in consideration of their anionic nature, a cationic resin must be used if the fiber is to be penetrated by the resin. It is obvious however, that regardless of how well the process is controlled, some degree of direct fiber bonding will result from inter-fiber precipitation.

The implication is therefore, that some reduction of softness will occur with the incorporation of either urea-formaldehyde or melamine-formaldehyde resins in a sheet.

ABSORBENCY

"Absorbency is defined (10) as that property of a material which causes it to imbibe or take up liquids with which it is in contact. Several measures of absorbency are:

a. The time required for the material to take up a specified volume of the liquid.

b. The rate of rise of liquid along a vertical strip dipping into the liquid.

c. The area of a specimen wetted in a specified time.

d. The total absorptive capacity expressed in terms of the quantity of liquid taken up by a completely saturated sample. The method of measurement of absorbency of paper depends importantly upon the specific use of the paper.

Absorbency in bibulous papers is commonly measured by the time of complete absorption of .1 ml. of distilled water as described by TAPPI standard T 432m-45. The end point in this test is determined by a cessation of light reflectance from the unabsorbed liquid upon the surface of the specimen. In the case of a highly absorptive sheet such as facial tissue or blotter stock, the end point would be so rapid as to increase the human error beyond reasonable limits of accuracy. A far more accurate absorbency test for this type of paper would be one dtermining the rate of rise of a liquid along a vertical strip dipping into the liquid. This test would allow a more practical end point with accurate results.

Many sources (9,17,18,) report the use of urea-formaldehyde and melamine-formaldehyde resins in absorbent papers, particularly toweling stock. Although there seems to be little doubt that some reduction in absorbency occurs, the widespread use of resins in absorbent products would indicate that the characteristic is not too adversely effected. Collins and Adrian (17) report that the melamine resin decreases absorbency more than the urea resin, although neither are too extreme in their effects.

Gruntfest and Young (3) investigated the effects of polymeric and monomeric resins upon absorbency, and find that since absorbency is primarily a capillary or inter-fibre phenomenon, there is far less reduction in absorbency on the monomeric level. They plot absorbency against wet strength

with urea-formaldehyde and melamine-formaldehyde resins of high and low polymerization, and show a 1000% increase in absorption time (by TAPPI T 432m-45) on the polymeric level. There is also conformation that urea resin retains absorbency more efficiently than the melamine resin.

Since the efficaciousness of a resin as a wet strength agent is dependent to a large degree upon it's polymerization, numerous wetting agents are available to offset the sizing effect of high polymeric precipitation. Schur (19) suggests wetting agents such as "Indrapid" and "Nekal A", and a manufacturer (16) combines softening ingredients with a powerful wetting agent to combat "water repellent resin films".

A leading producer of urea-formaldehyde resin reports (20) that manufacturers of absorbent papers frequently object to the loss of absorbency caused by alum. Since anionic resins require alum as a mordanting agent, the subsequent loss of absorbency with this type of resin would discourage its use from this standpoint. The same producer has announced a new urea-formaldehyde resin which is modified to control condensation and cationic properties. This resin is said to be capable of conferring high absorbency to the finished sheet.

STRENGTH CHARACTERISTICS

To visualize the effects of resins upon the strength characteristics of paper, it is necessary to start with a theory of reaction. Collins and Adrian, in their review (17) of wet strength mechanisms, present two theories.

These two theories were originally promulgated by Steenberg, to account for the phenomenon of wet strength reactions.

First, the strength connected to occurence of hydrogen bridges between hydroxyl groups should be considered. If no resin is present, these bridges are broken by water. In a treated pulp, the resin forms an insoluble ether linkage between the molecules.

The second theory assumes that the cured resin in the sheet, covers the most swellable fiber parts, so that the stresses created in the drying of the gel cannot relax when the sheet is wetted.

Landes and Maxwell (8) confirm Steenberg's theory with findings that the ultimate strength of individual fibers are "improved only moderately or not at all", whereas fiber to fiber bonding is strengthened considerably.

Wet strength is evaluated by TAPPI standard T 456m-49, wherein a distinction is drawn between normal wet strength and ultimate wet strength. Ultimate wet strength means the strength of a material after complete saturation, while normal wet strength is the strength possessed by a material after it has been wetted to an extent comparable with normal use conditions.

Britt (17) defines a wet strength paper as one which has a wet tensile of at least 15% or more of the dry tensile strength. This is computed at complete saturation. The increment is easily attained as numerous sources (21) (22) report wet tensiles as high as 60% of the original dry tensile, along with somewhat comparable increases in other strength capacities.

Since wet strength resins measurably improve fiber to fiber bonding, upon which sheet strength is dependent, it is only natural that dry strength be increased. However, it must be emphasized that dry strength is controlled to a great extent by the degree of polymerization of the resin, and its

disposition on the fiber. One source (3) finds a difference of as much as 50% in dry strength between polymeric resins and monomeric resins. These findings are based upon both melamine-formaldehyde resins and urea-formaldehyde resins. Actually it has been shown conclusively (3) (23), that the intrinsic capacities of urea and melamine resins to improve the strength properties of paper are entirely equivalent. This, however, is not apparent immediately off the paper machine, due to the recognized (8) (9) fact that melamine resin cures faster than urea resin.

In view of the incremental dry strength performance of resin treated papers, it has been suggested (25), that resins offer interesting possibilties in the direction of lower basis weights and cheaper fibers. In some instances the savings in fiber weight or cost would more than offset the cost of wet strength chemicals. Paper towels are an example of a sheet that frequently can be made in lower basis weights when treated with resins.

SUMMARY

It is evident from this study that the use of melamine-formaldehyde or urea-formaldehyde resins will incur some losses in softness and absorbency. This decrement can undoubtably be mitigated by careful supervision of the degree of condensation. Condensation is best controlled by the viscosity and concentration of the resin solution.

Dry strength is improved by resin action, although less outstanding in the monomeric range. Application of the low condensed resin is however,

necessary to retain softness and absorbency.

Urea and melamine resins are about equivalent in strength contributions, although the melamine resin develops wet strength faster than the urea resin. Mention might be made that melamine resins are more expensive than urea resins.

Pulp is anionic in nature, and is attracted to a cationic resin without a mordant such as alum. Since alum decreases absorbency, the use of a cationic resin is favored.

-END-

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EXPERIMENTAL

The purpose of the laboratory investigation was to determine quantitatively, what decreases in softness and absorbency would accompany wet strength. A typical urea- and melamine-formaldehyde resin was chosen for the production of wet strength.

The melamine resin was prepared for use by the addition of powdered resin to a 1.5% solution of HCl in the final proportion of one mole of resin (as monomer) to .8 mole of HCl. The solution was aged for 24 hours before use. Such a solution contains .765 grs. of resin per cc. of solution; therefore it was diluted to contain .025 grs. of resin per cc. for practical administration to the fiber suspensions.

The urea resin used was of the cationic type co-reacted with sodium bisulfite for increased solubility. It was obtained in a water solution containing 28.4% resin solution of solids and was also diluted to .025 grs. resin per cc.

A typical sulfite pulp was beaten and disintegrated as prescribed by TAPPI Standards. This same batch of pulp was used throughout the investigation so that inherent physical qualities could be maintained constant.

The sheet making procedure was as follows. A standard TAPPI sheet mold was used with two burettes mounted above it. Eight hundred ml. of pulp was added to the mold at 1.75% consistency, yielding a sheet weight of 1.25 grams. The suspension was acidified with H_2SO_4 from one burette to a pH of 4.5, and the resin solution was added from the other burette. A contact time of one minute was allowed and then the sheet was made, couched, and pressed. This procedure was done according to TAPPI T 220 m50.

Drying was done under a canvas blanket and a blotter on a photographic print drier operated 180 to 200 degrees F. Drying at this temperature for a period of 90 seconds was the only curing applied to the sheet. The sheets were then racked in the constant humidity room and allowed to age for one week.

After a period of one week, the conditioned sheets were tested for wet and dry tensile, absorbency, softness, and dry tear. All properties were evaluated in the conventional manner with the exception of absorbency. The TAPPI method of evaluating absorbency yielded poor results due to an end point which was far too rapid to be accurately recorded. Instead, a Finch device was mounted in a tensile tester and a one half inch strip placed in the device in the usual manner. Absorbency was then measured by the intervals of time required for the water to rise to height of one and one half inches. The reproducibility of this test proved to excellent. Softness was evaluated with a Clark softness tester and good correlation was found with subjective tests. All the wet tensile data was obtained with a Finch device using a controlled soak of five minutes.

RESULTS

The effects of resin treatment are shown in tables I thru IV. Tables I and II show the actual values obtained with the testing instruments, whereas Tables III and IV indicate the per cent variation of the actual values.

Since the magnitude of the actual values are specific to the particular pulp used, they are of value only to the extent that their

per cent increments illustrate the influence of the corresponding increase in resin treatment. All per centage figures are based upon the values obtained from the untreated sheets prepared at a pH of 4.5. The values shown represent the average obtained from a minimum of five samples for each value. The per centage variations for urea and melamine resins are graphically represented in Figs. 1 and 2 respectively.

It is evident from both Figs. 1 and 2, that absorbency suffers far more decrement than does softness; the effect being more pronounced with the melamine resin. A side effect such as a 400% reduction in absorbency must be seriously reckoned with if a resin treated sheet is to be used for such a product as a facial tissue. Possibly some absorbency might be restored by the application of wetting agents.

The softness values shown in Tables I and II represent the critical length in centimeters necessary to flop a two inch strip over in a ninety degree arc on a Clark softness tester. These values were not converted to Clark's softness formulars because all tests were conducted with similiar sheets of the same basis weight of 62.5 grams per square meter. Thus the critical lengths may be directly compared to each other. Figs. 1 and 2 show that softness can be reduced form 100 to 125% by a three per cent resin treatment; the effect is again more pronounced with the melamine resin. Where softness is of prime importance, its reduction must be mitigated in a resin treated sheet or the value loss will surmount the value gain. A softening oil such as ethylene glycol might be utilized for this purpose.

The advantageous results of resin reaction, particularly the 45 to 50% increase in wet tensile are contrasted in Figs. 1 and 2. It is these desireable increments, and to a lesser extent those of tear and dry tensile, which justify wet strength treatment. However, Figs. 1 and 2 show that the reductions in softness and absorbency increase rapidly beyond a 1.5% resin treatment, while the strength gains at that point are still substantial. Therefore, a 1.5% resin treatment is felt to be the optimum operating level for a wet strength facial tissue. This represents a compromise between gain and loss at a point where value gain is greater than value loss.

From this particular investigation it would seem that the urea resin is a better choice than the melamine resin, however this should be confirmed by actual mill trial, since resin performance might be varied by practical considerations.

SUMMARY

Sheets were prepared with varied resin treatment and tested for resin effect upon physical characteristics. Softness and absorbency were found to have been drastically at 3% resin contact, while at 1.5% the reductions were acceptable in view of the wet strength increases. Therefore at lower concentration ranges, the use of urea and melamine resins are not considered to be too inimical to a soft absorbent sheet. The urea resin is apparently more desireable than the melamine resin

DATA

TABLE I ACTUAL VALUES - MELAMINE RESIN

PER CENT RESIN TREAT.	WET TENSILE lbs./in.	DRY TENSILE lbs./in.	ABSORBENCY secs.	SOFTNESS cm.	TEAR grs.
0.	0.	12.0	81	2.1	38.3
0.5	3.1	12.8	96	2.2	39.0
1.0	4.2	13.8	142	2.45	39.5
1.5	4.6	14.3	173	2.85	40.2
2.0	5.2	14.8	246	3.4	40.6
2.5	5.6	15.3	321	4.0	41.4
3.0	6.0	15.6	456	4.75	44.0

TABLE II ACTUAL VALUES - UREA RESIN

PER CENT RESIN TREAT.	WET TENSILE lbs./in.	DRY TENSILE lbs./in.	ABSORBENCY secs.	SOFTNESS cm.	TEAR grs.
0.	0.	12.0	81	2.1	38.3
0.5	2.2	13.1	88	2.6	39.1
1.0	3.3	13.8	112	2.9	39.5
1.5	4.1	14.3	147	3.15	40.2
2.0	4.7	14.7	192	3.45	40.9
2.5	5.2	14.9	256	3.7	42.0
3.0	5.5	15.1	347	4.25	43.4

TABLE III PER CENT VARIATION - MELAMINE RESIN

PER CENT RESIN TREAT.	% INCREASE WET TENSILE	% INCREASE DRY TENSILE	% DECREASE ABSORBENCY	% DECREASE SOFTNESS	% INCREASE TEAR
0.	0	0	0	0	0
0.5	25.0	6.6	18.5	5.1	2.2
1.0	33.3	13.0	75.0	17.5	3.4
1.5	38.4	19.2	113.0	37.9	5.1
2.0	43.4	23.4	203	60.6	6.3
2.5	46.5	27.4	296	90.2	8.0
3.0	50.2	30.2	462	126.2	14.7

TABLE IV PER CENT VARIATION - UREA RESIN

PER CENT RESIN TREAT.	% INCREASE WET TENSILE	% INCREASE DRY TENSILE	% DECREASE ABSORBENCY	% DECREASE SOFTNESS	% INCREASE TEAR
0.	0	0	0	0	0
0.5	19.2	9.6	8.6	24.3	2.3
1.0	25.8	15.0	38.2	38.0	3.4
1.5	34.2	19.2	73.5	51.2	5.1
2.0	38.2	22.0	137	64.8	6.6
2.5	42.5	24.4	216	76.3	9.7
3.0	45.0	25.8	328	110	12.6

FIG. 1

PER CENT VARIATION Vs. PER CENT UREA RESIN

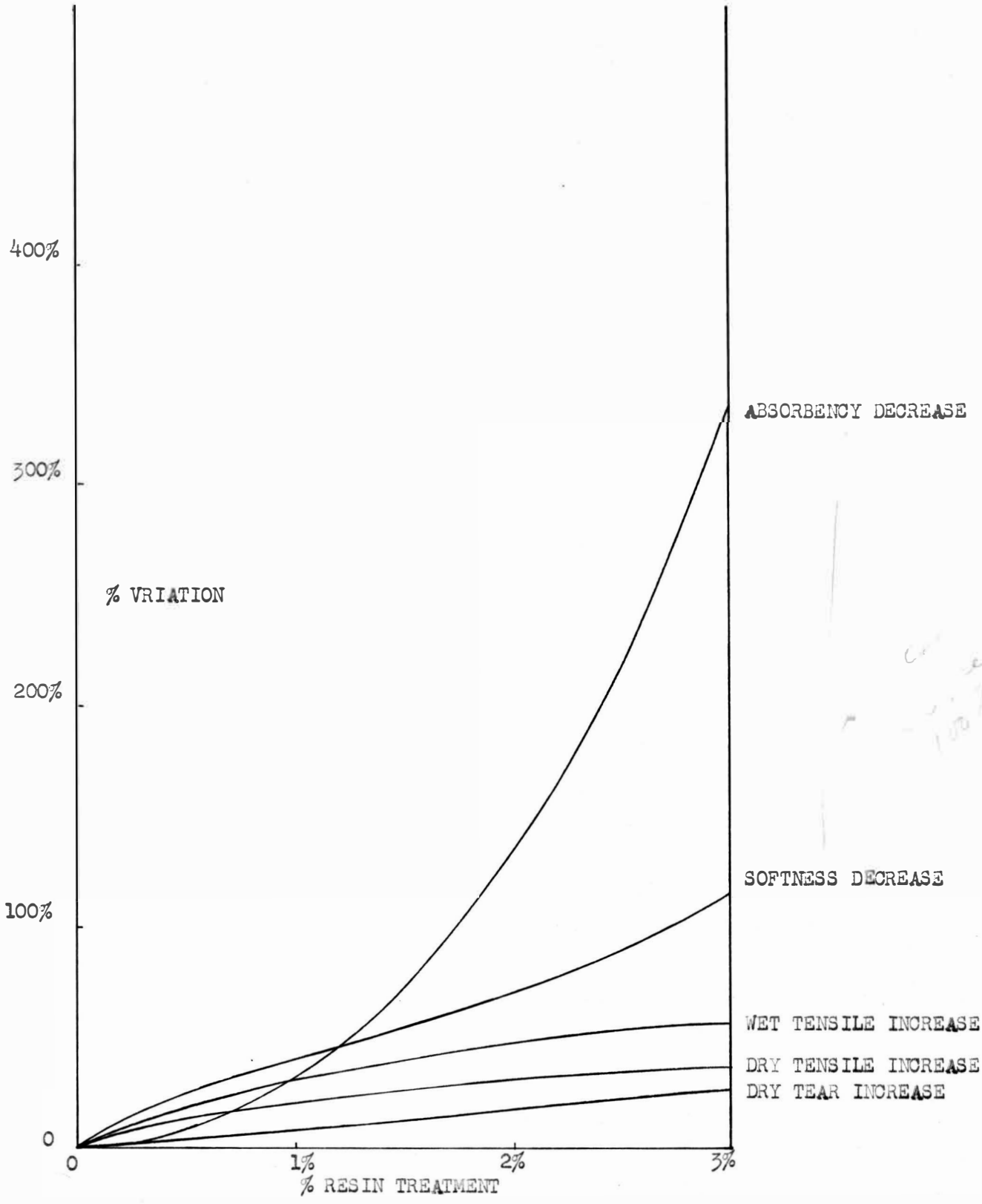

FIG. 2

PER CENT VARIATION Vs. PER CENT MELAMINE RESIN