Study of Beater Additives

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Introduction

During the last fifteen years there has been considerable interest and activity in beater saturation or beater additives due to the great number of materials that have been developed by the various manufacturers. These materials are in the line of synthetic rubbers, copolymers and various kinds of resins which are all available in the form of emulsions or latices that can be used in the beater addition process. Thermosetting, thermoplastic, elastomeric and resinous materials are all currently being used to develop a wide variety of properties in the finished paper sheet.

The use of Melamine formaldehyde and other thermosetting resins for producing wet strength paper has grown steadily in the last decade. The growth has been possible through improvements and modifications of these resins. These relatively highly condensed resins exhibit an affinity for cellulose fibres directly or through an alum when water solubility is imparted to them.

Application of water dispersible derivatives of cellulose and starch is not new. It is known to papermakers since a long time that the addition of water soluble gums to pulp improves the strength and other physical properties of paper. The recent interest in natural and synthetic gums as beater additives has been not only for the improvement of strength properties and formation of paper but also as an aid to rosin on engine sizing.

The work done so far on beater additives or the new developments in paper technology mostly confine to wood pulp. The reason is quite obvious and apparent as wood constitutes the chief raw material for paper making in Western countries. Bamboo is the most important raw material for paper making in India, hence following studies have been based on bamboo pulp. An attempt has been made in the present article to study the effect and mechanism of various type of natural and synthetic gums, thermosetting rèsins on the retention of fillers, degree of sizing and the mechanical strength of paper produced from bleached bamboo pulp.

The article is presented in parts. The first part of the article contains natural and synthetic gums as beater additive and its second part deals with the reagents for imparting wet strength to papers.

PART I

Studies on natural and synthetic gums as beater additives

Three types of gums belonging to three different categories were selected for these studies. Their names, along with their salient features are given below:

1. Starch Märk	:	Commercial grade.
Suppliers	:	Anil Starch Products, Ahmedabad.
2. Artificial gum	:	Carboxymethyl cellulose (CMC)
Mark	:	CEKOL MV
Suppliers	:	Cellulose Products of India Ltd.
Viscosity of 1% solution	:	185 cps (measured by Brookfield viscometer).

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Wet end addition of small amounts of carboxymethyl cellulose has been reported to give the following improvements under various conditions: Increased bursting and tensile strength, increased tear strength, improved formation, improved retention of fillers and better sizing.

3. Vegetable gum	:	Guar Gum
Mark	:	Glacoid P
Suppliers	:	Modern Engineering Works, Calcutta.
Viscosity of 1% solution	:	480 cps. (measured by Brookfield Viscometer).

The particular type of product under consideration is composed of galactomannan gum guar, the cold water soluble carbohydrate of the guar seed. There are many other type of gums available in the market which have their own specific use, but out of them guar gum is most intersting owing to its multiple advantages. Cushing reports that when guar gum is present in the stock preparation waters before beating or refining it makes the stock faster draining with high strength values than normal. If further results in improvement of formation, better sizing and surface uniformity.

It will not be out of way to give in short the mechanism of retention of these polymers on cellulose fibres. Starches, vegetable gums impart strength to paper by virtue of their ability to improve the bonding between cellulose fibres—that is, they serve as interfibre adhesives. Various factors that influence the strength of sheet, when the above materials are used as beater saturants, are:

(a) The strength of adhesive bonds between the cellulose and the material.

(b) The chain length or degree of pollymerisation of the gum.

(c) The strength of cohesive bonds between the molecules.

The molecules of starch or gum are first absorbed onto the surface of cellulose fibres in order to have effective fibre to fibre bonding. The hydroxyl bonds on the surface of the fibres, which otherwise are not taking part in the inter molecular bonding, then form interfibre linkages. However, the mechanism of CMC is slightly different. Molecular structure of CMC usually approximates that of unmodified cellulose as a result the internal additive, although it in water soluble, develops a fibre bonding efficiency of high order and further on absorption impart high mechanical strength to fibres. Carboxymethyl cellulose possesses no sizing properties in itself but it acts as a protective colloid to prevent agglomeration of the size particles in presence of alum *i.e.* at a low pH value around 5.0.

Experimental procedure

Bleached bamboo pulp was defiberized and lightly beaten in a valley laboratory beater at a consistency of 1.8 percent to a freeness of 45° Schopper Riegler. The

Bleached bamboo pulp was defibrized resin and pH adjusted to 5.5-6.0 with appropriate quantity of alum solution. Before addition of the rosin size in beater, 5.0 per cent china clay on pulp was also added. Portions corresponding to 25 grams of pulp were taken and mixed for ten minutes with the proper amount of the material under study before being formed into sheets on the standard British sheet making machine. Basis weight of the sheets made was strictly controlled and kept at 60 ± 1 gms/sq.m.

(In all the cases the additives were added to the pulp slurry in the form of solution of 1 per cent consistency).

Strength properties of the paper sheet thus made were determined according to TAPPI standards.

Results of starch, CMC and guar gum are produced in the following tables 1, 2 and 3 respectively.

Graphical representation of the percentage amount of the material on pulp against percentage rise or improvement in strength properties are shown in Figures I, II and III.

Discussion

The effect of varying starch proportions on the dry strength properties of paper, ash of paper and degree of sizing *i.e.* cobb value are shown in Table No. 1.

As can be seen from the table the ash content of paper steadily increases indicating higher retention of fillers while the cobb value decrease with higher amounts of starch. So far the strength properties are concerned in the beginning the percentage improvement in strength is sharp but it becomes almost stationery at the later stages. The limit after which no substantial rise in strength occurs is at 1.5 per cent.

Table 1

S. No.	% Starch added on b. d. pulp	Burst Factor	Breaking length m.	Tear Factor	Ash in Paper %	Cobb value
1.	nil	30.10	3950	58.80	2.40	39
2.	0.5	31.53	4000	60.80	2.61	34
3.	1.0	32.23	4145	62.62	2.80	32
4.	1.5	32.64	4200	63.52	2.87	28
5.	2.0	32.81	4240	65.81	2.92	27
6.	2.5	33.20	4250	65.25	3.10	24

FIGURE I

STARCH ON PULP VS IMPROVEMENT IN STRENGTH

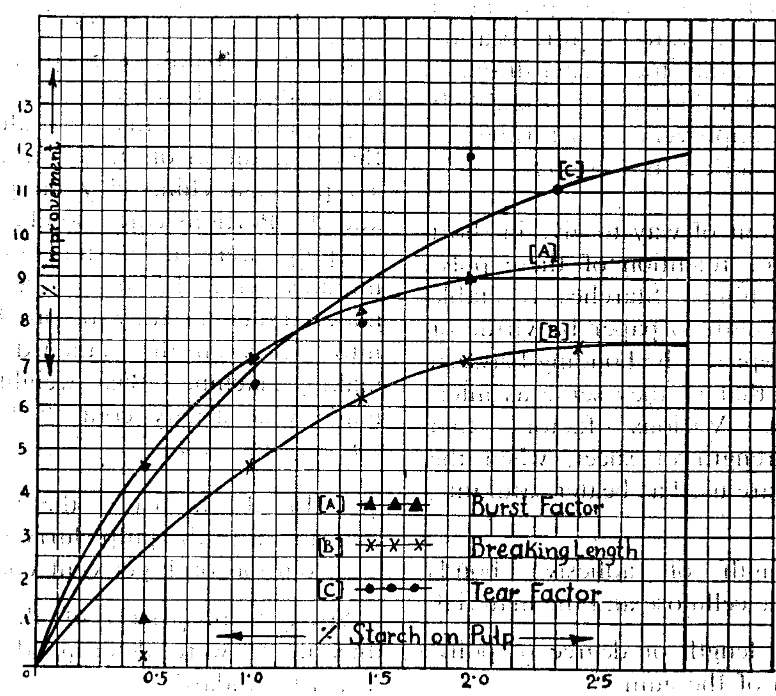


Table 2

S. No.	% CMC added on b. d. pulp	Burst Factor	Breaking length m.	Tear Factor	Ash of paper %	Cobb value
1.	nil	31.70	4105	60.00	2.30	42
2.	0.5	34.02	4333	62.28	2.42	38
3.	1.0	35.10	4484	64.15	2.52	32
4.	1.5	35.70	4585	64.98	2.79	30
5.	2.0	36.35	4650	65.46	2.98	28
6.	2.5	36.76	4635	66.00	3.20	26

Table No. 2 gives the results for carboxymethyl cellulose.

The effect of varying amount of CMC on various characteristics, namely: strength properties of paper, ash (an indirect measure of retention) and cobb value, is well marked as apparent from the above table and Figure No. II.

Though, the trend of curves in case of CMC is same as what has been observed in case of starch, but the percentage rise in strength is very quick in the initial stages-- that is up to 1.5 per cent (Figure II). The decrease in cobb value and the increase in ash contents are approximately of the same order as in starch.

Table 3 contains the strength properties, ash and cobb value of paper saturated with guar gum.

FIGURE II

CMC ON PULP VS. IMPROVEMENT IN STRENGTH

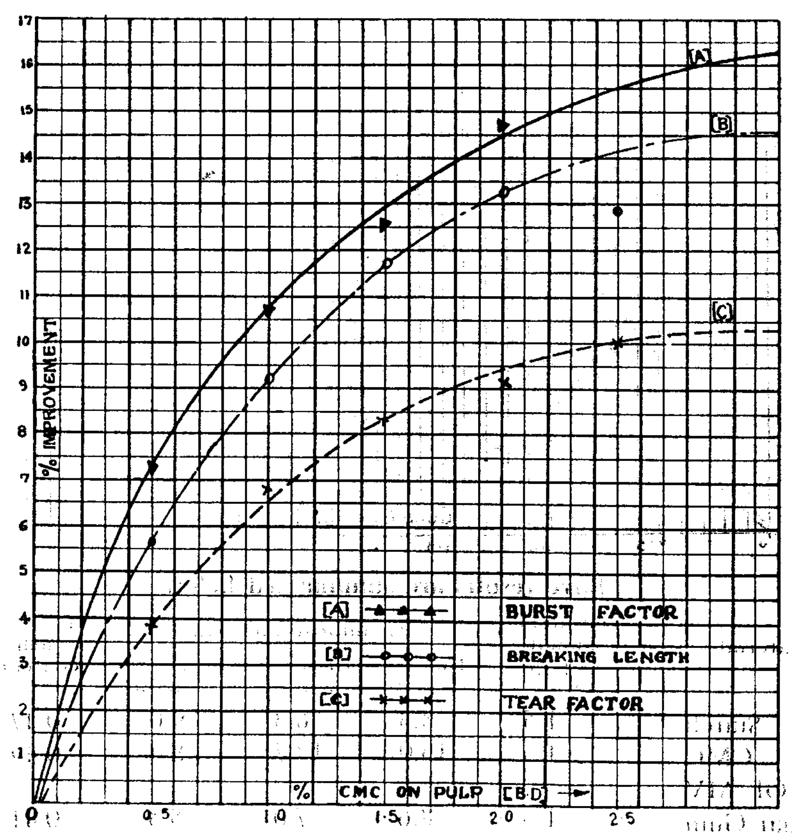


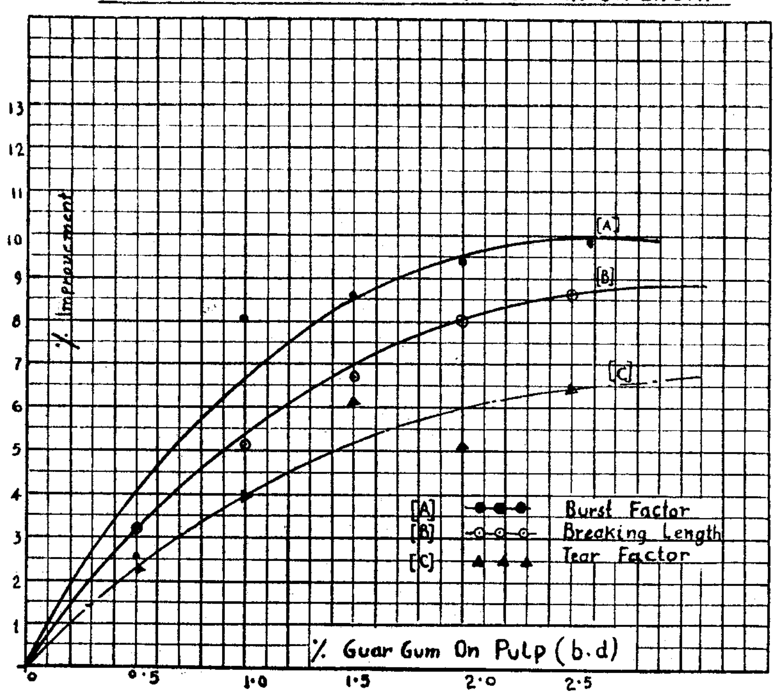
Table 3

S. No.	% Guar gum added on b. d. pulp	Burst Factor	Breaking length m.	Tear Factor	Ash of paper %	Cobb value
1.	nil	32.82	4100	63.70	2.46	43
2.	0.5	33.67	4231	65.10	2.79	35
3.	1.0	35.45	4313	66.25	2.81	28
4.	1.5	35.65	4379	67.65	2.87	23
5.	2.0	35.95	4428	67.08	2.92	22
6.	2.5	36.10	4463	67.85	3.00	20

As apparent from the above table the improvement in mechanical strength of paper is somewhat on the lower side as compared to the value obtained with starch or CMC. But the position is different with the cobb value. In this case, the cobb value is lower than the corresponding figures of starch or CMC. In the early stages the percentage rise in strength of paper is slow unlike paper treated with starch or CMC—where the rise is sudden and appreciable. In all the cases the shape of curves remains basically the same (Figure III). Examination of the curves reveals that there is hardly any improvement in mechanical strength after 1.5 per cent guar gum addition.

FIGURE III

GUAR GUM ON PULP VS IMPROVEMENT IN STRENGTH



Above results are summarised below

S. No.	Material	Optimum amount on pllp %	% improvement in Burst Factor	% improvement in Breaking length	% improvement in Tear Factor	Rise in ash contents	Decrease in cobb value
1.	Starch	1.5	8.3	6.3	9.0	0.47	11
2.	CMC CEKOL MV	1.5	13.0	12.7	8.3	0.49	12
3.	Guar Gum	1.5	8.6	7.0	5.3	0.41	20

From this summary it is inferred that Guar gum gives a very good degree in sizing *i.e.* decrease in cobb value, whereas the percentage improvement in strength is best with carboxy-methyl cellulose. At the optimum quantity of 1.5 the ash contents in paper are same in all the cases.

PART II

Reagents imparting wet strength to papers

The effect of thermosetting resins on the dry and wet strength of paper has been the subject of considerable study in the past few years. Workers in the field include Stennet [3], [4], [7], [9], Swanson[2], Goldstein, Linke[5] Cushing[6], Baymiller." These scientists have studied beater saturants from different angles and lot of work has been published on different resins belonging to different group.

The present article is confined only to Melamine Formaldehyde—the parent material belonging to thermosetting series of resins—and its action on wet strength properties of bamboo paper.

The mechanism of retention of this resin and wet strength development may be explained in broad terms on the following lines. According to Linke the cationic melamine polymer is absorbed on the anionic cellulose surface and the phenomenon of thermosetting occurs under normal paper drying conditions. The polymer becomes crosslinked and insoluble upon heating, bonds both to itself and to the cellulose and splits off water and formaldehyde. Wet strength results through the formation of resin bonds which are not sensitive to water and by a protective 'Shielding' of the cellulose and cellulose hydrogen bonds.

Material and Method

Resin 'CIBA' 286 used in the present studies is a melamine formaldehyde resin available in fine white powder form. The resin is soluble in a limited amount of warm water and in dilute hydrochloric acid. The suppliers of this resin are CIBA of India Ltd., Bombay.

Preparation of the resin solution

4.5 ml. of the hydrochloric acid (20° Be) are added to 100 ml of water. 15 grams of the resin is then added into the acid water solution at 40°C with constant agitation for at least 15 minutes. Further, 45 ml. of water are added to give a resin solution of 1 per cent concentration.

Procedure

The bleached bamboo pulp was processed in the same manner as mentioned in the experimental procedure of Part I.

Beaten pulp slurry equivalent to 25 grams of pulp (1.8 per cent consistency) of pH around 5 was taken in a mixer and requisite volume of 1 per cent resin solution added The mass was then stirred vigorously for 5 minutes before standard sheets were made in British sheet machine.

Varying proportions of resin on pulp were tried with a view to see the effect of varying concentration of M. F. on wet and dry strength of paper.

Wet strength of paper was determined in the following way:

The standard paper sheet was dipped in water at room temperature for exactly 5 or 10 minutes. At the end, surface water was wiped off by means of a blotting paper and strength properties determined in the usual way.

Dry and wet strength properties of the paper are shown in Table 4.

Table 4

Table Sub-division	Treatment (Bleached) bamboo pulp+resin)	% Malamine formaldehyde on b.d. pulp	Basis weight	Burst Factor	Breaking length m.	Tear Factor
4—A	Dry strength properties.	nil	60.7	36.16	4438	57.55
		0.5	60.4	37.10	4518	58.78
		1.0	59.6	38.40	4767	61.65
		1.5	59.8	38.80	4906	63.30
		2.0	60.7	39.40	4989	63.24
		2.5	60.9	40.22	5120	65.80
4—B	Wet strength after dropping the sheet in water for 5 *minutes.*	nil	58.9	2.30	383	-
		0.5	59.3	5.00	552	-
		1.0	59.6	6.83	765	-
		1.5	59.3	7.85	923	-
		2.0	60.1	8.11	971	-
		2.5	60.3	8.25	955	-
4—C	Wet strength after dropping the sheet in water for 10 *minutes.*	nil	59.7	2.12	212	-
		0.5	60.2	3.66	424	-
		1.0	60.15	5.26	572	-
		1.5	61.00	6.60	658	-
		2.0	60.82	7.16	699	-
		2.5	60.7	7.27	695	-
4—D	24 *hrs.* curing at 95°C and then dipping in water for 5 *minutes.*	nil	60.2	2.11	364	-
		0.5	60.12	10.40	978	-
		1.0	59.70	16.70	1510	-
		1.5	59.53	19.00	1660	-
		2.0	60.71	18.30	1850	-
		2.5	60.9	17.60	1580	-
4—E	48 *hrs.* curing at 95°C and then dipping in water for 5 *minutes.*	nil	59.5	2.05	231	-
		0.5	59.6	10.65	983	-
		1.0	60.12	18.60	1920	-
		1.5	60.3	17.20	1960	-
		2.0	60.2	18.70	2100	-
		2.5	59.9	17.7	1780	-

The percentage improvement in dry strength of paper is quite sharp in the initial stages that is up to 1 per cent but with higher amount of the resin the percentage rise in the strength is not very prominent compared to the amount of resin added. The optimum increment in strength was obtained at 1.5 per cent resin on pulp (Figure IV and Table 4-A).

But, the picture is different when wet strength of paper is examined, (Tables 4-B and 4-C). As expected, the increase in quantity of resin invariably results in rise of wet strength of paper. The rise is well marked and very prominent up to the level of 1 per cent resin (on pulp). Thus, even in the uncured state the paper treated with M.F. resin possesses high wet strength. This is because of its hydrophobic nature and high molecular weight.

The curves in Figure V, which show the relationship between the percentage M.F. resin on pulp and percentage of the original strength retained (on dipping the sheet in water), have a remarkable similarity. These curves reach to a peak value before they start descending,—indicating that only a certain percentage of melamine resin is effective in maintaining, to a good degree, the original strength of paper. It may be inferred from these curves that the maximum retention of the original strength, to the extent of 21 per cent, is possibly only at 1.5 per cent M.F. resin. What has been said above holds good for 5 minutes or 10 minutes wet strength though in the later case lower retention value of the initial strength is obtained.

FIGURE IV

MELAMINE FORMALDEHYDE RESIN ON PULP VS. IMPROVEMENT IN STRENGTH

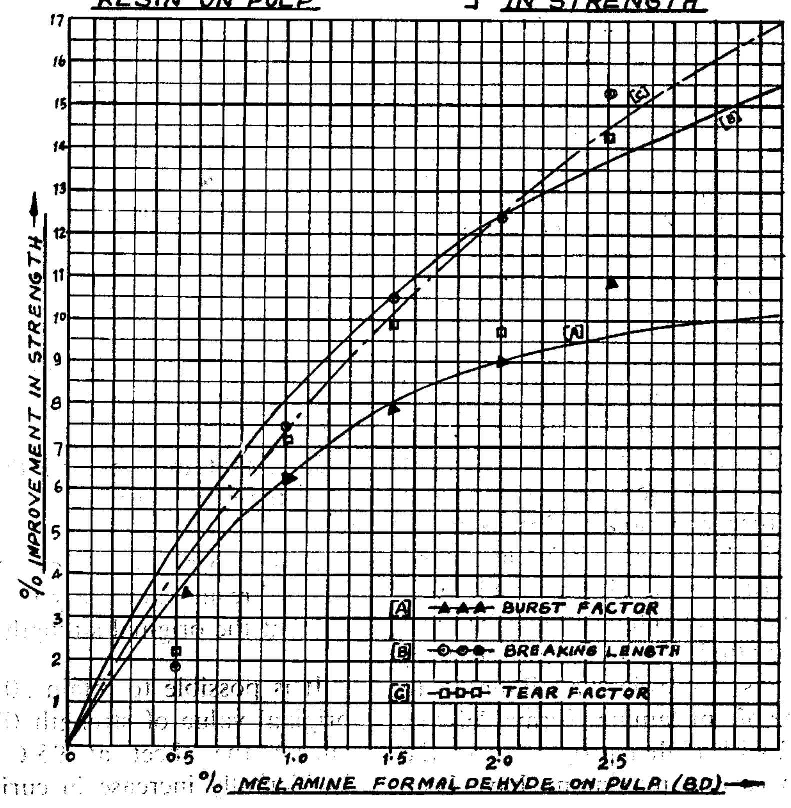


FIGURE V

MELAMINE FORMALDEHYDE ON PULP (BD) VS. STRENGTH RETAINED (AFTER DROPPING THE SHEET IN WATER)

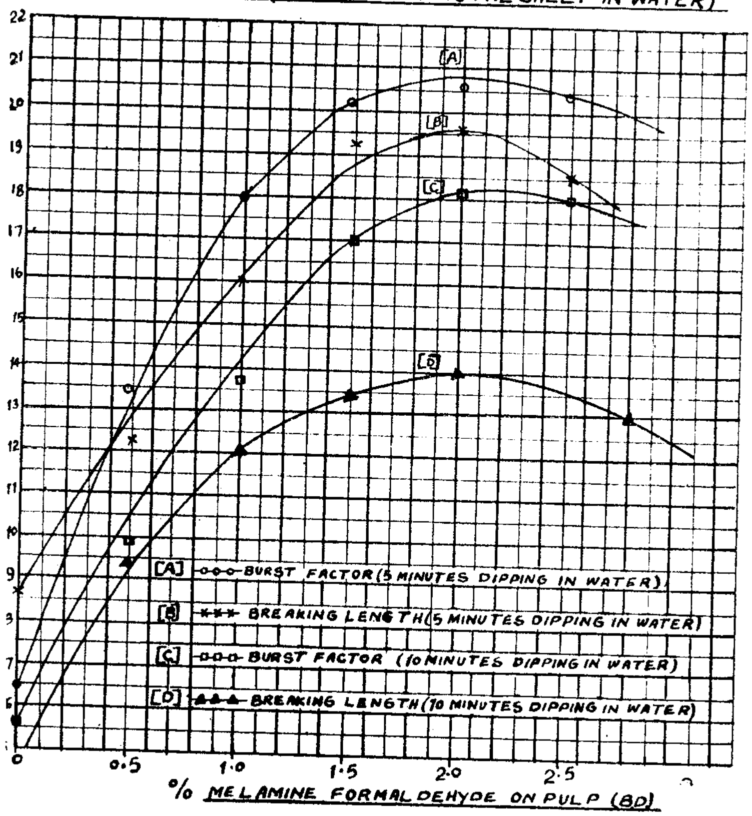
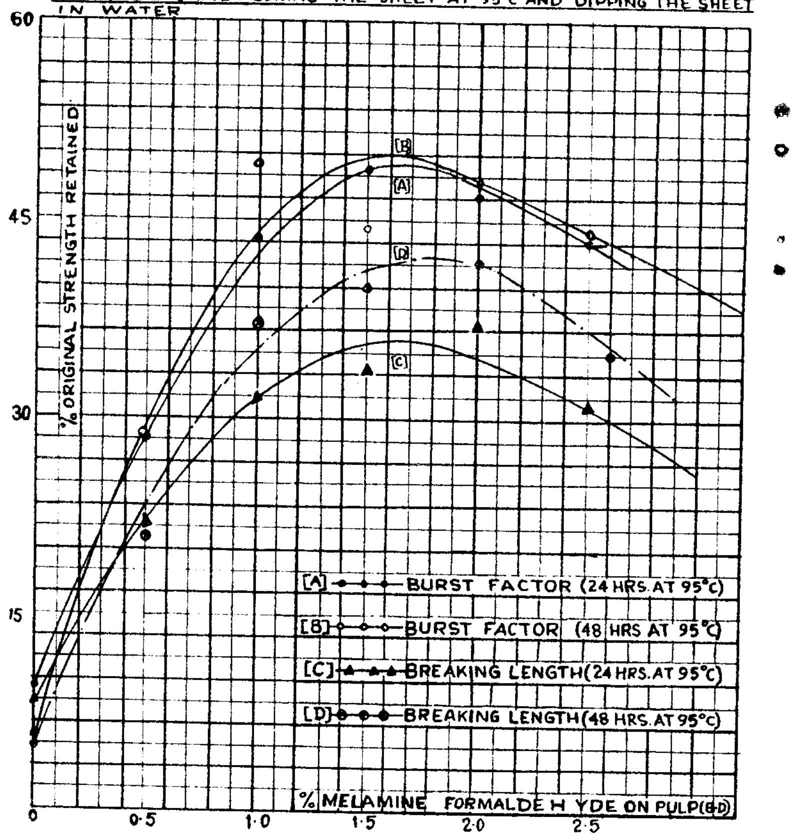


FIGURE VI

MELAMINE FORMALDEHYDE ON PULP (B D) VS STRENGTH RETAINED (AFTER CURING THE SHEET AT 95°C AND DIPPING THE SHEET IN WATER



Effects of curing the sheet on wet strength are shown in Tables 4-D and 4-E, and percentage of the strength retained against varying amounts of resin are shown diagramatically in Figure VI.

The effect of curing on melamine formaldehyde treated paper is essentially what could be expected on the basis of the property of this polymer. Earlier, it was observed that there was no significant change in wet strength properties of the untreated sheets on curing and, therefore, it was concluded that any change in the wet strength of treated sheets from those of untreated sheets was solely attributable to the presence of melamine formaldehyde. Paper treated with higher proportion of the resin up to a certain maximum, have been found to develop greater wet strength on curing than the papers treated with a lower amount of the resin (Figure VI).

Again, there is a very good similarity in figures V and VI; these curves resemble especially in the following respects:

1. Type of curves.
2. Extent in rise, and the uniformity in the rising curves.
3. The peak value *i.e.* maximum amount of resin—necessary to retain maximum of the original strength—is 1.5 percent.

It is possible to retain 50 per cent of the original value of strength (Burst Factor) on curing the sheet at 95°C for 24 hours. Incidentally increase in curing time beyond 24 hours hardly gives any advantage

(Figure VI). Perhaps, the time of curing could be minimised if the M. F. treated papers are cured at high temperature. Experiments in this field are in progress.

Further work with other resins is in progress. The results will be communicated in the forth coming issues of IPPTA magazine.

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