Effect of filler modification on sizing and printing properties

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ABSTRACT

Internal sizing, porosity anp printability properties of hand sheets made with bamboo, eucalyptus and their mixed pulps have been evaluated. Talc and alumina hydrate have been used as filler materials. Structural modification brought out in the fillers, has been explained through the thermal analysis data. The filler loading levels have been altered from 10 to 60% without retention aid and with cationic as neutral starch. The sizing and printability properties obtained with the four modifications in filling stage have been compared. The properties have been interpreted based on the porosity values and theoretical considerations.

Fossibility of superior optical and strength properties with more flexibility in filler selection meeting requirements for printing, absorbancy and fire retardancy has been explained on using calcined alumina hydrate, compared to conventional fillers. The cost and quality factors have been discussed vis a vis industrial applications.

Introduction :

Use of thermal treated filler or coating materials, notably talc and alumina hydrate, has rarely been attempted in manufacturing of quality paper though extensive work has been carried out on thermal treatment of kaolinite clay for both filling and coating (1,2). The reason for lack of literature may be because of the fact that talc is not used as common filler in Western countries and alumina hydrate is yet to receive wide attention as filler material unlike kaolinite. Alumina hydrate has however, found ample application as coating material. It was conceived, therefore, that apart from fundamental, it may be of commercial interest to undertake the present study.

It was predicted recently (3) that with the likely increase in production of alumina hydrate by about three times in the coming years in India and with the addition of some R and D works on diversification for paper manufacturing, cost of alumina hydrate may come out to be competitive with other coating and fill r materials. The wide range of pH where alumina hydrate can be used (4.5 to 8) is rarely achievable by any other filler materials in sizing process of paper manufacturing (4).

It was also shown that alumina hydrate imparts superior strength and bonding properties over other materials even at higher loading (5) "Super filled paper" (3).

Efforts are going on in our laboratory for possible use of alumina hydrate filled papers for cigarettes, fire retardant and many other functional papers. The present work has also allowed to emanate some of the basic findings in paper formation vis a vis porosity and the Washburn equation (6).

Experimental :

Thermal analysis and filler preparation :

Thermal analysis (TG=thermogravimetry and DTG=differential thermogravimetry) of alumina hydrate, talc, titanium dioxide and clay has been carried out using a Perkin-Elmer thermal analyser upto a temperature of 940°C Alumina hydrate and talc are heated for 4 hours at 400°C, 600°C and 800°C in an

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electrical muffle furnace in air and used in the stock preparation.

Pulp and papemaking :

Bamboo (arundinacea) and eucalyptus (tereticornis) pulps are prepared following to kraft process and bleached by CEH sequence to a brightness level of 80 ±1% El. Disintegration, beating in a laboratory Valley beater, handsheet preparation were carried out following to standard Tappi procedures.

Stock preparation :

20g samples of pulp from the beater runs were dispersed in 2L of water. Rosin (1%) and alum were used for sizing and retention of fillers. Filler dose varied from 10% to 60% on W/W pulp basis. In the experiments with thermal treated fillers, the filler dose was kept at 20% w/w pulp basis.

Paper Testing :

All the handsheets were tested for fibre strength factor (FS factor) and bond factor (B-factor) in Pulmac trouble shooter (made in USA, Model TS—100). Porosity of the handsheets has been determined in Bendtsen smoothness and porosity tester and reported in ml/min. Internal sizing (Thiocyanate flotation method) has been tested following to Tappi UM-429. Printability (in terms of ink density) has been done in an IGT printability tester (Model A-1). Printability has been quantified by visual observation and comparison with suppliers standard strips.

Results and Discussion :

Four sets of modification have been carried out in the present work :

1 Calcination upto 800°C with 20% addition level.

2 Increasing filler loading from 10 to 60%.

3 Filler loading upto 50% with cationic starch.

4 Filler loading upto 50% with neutral starch.

Perusal of literature shows that the calcination of filler materials has been carried out without its implication on paper properties (7). It may therefore be worth presenting the thermograms of the fillers to find out whether the structural transformations, brought out in the fillers in course of thermal treatment, has any effect on the paper properties. Both the thermogravimetry (TG) and differential thermogravimetry (DTG) curves of alumina hydrate (Fig 1), clay (Fig. 2), titania and talc (Fig. 3) are shown here. The X-axis represents the weight percentage an Y-axis as temperature in °C The temperature studied ranges upto 940°C The TG results of different fillers are given in Table-1 showing the temperatures of peak, ranges of weight loss and ash content at the end of thermal analysis.

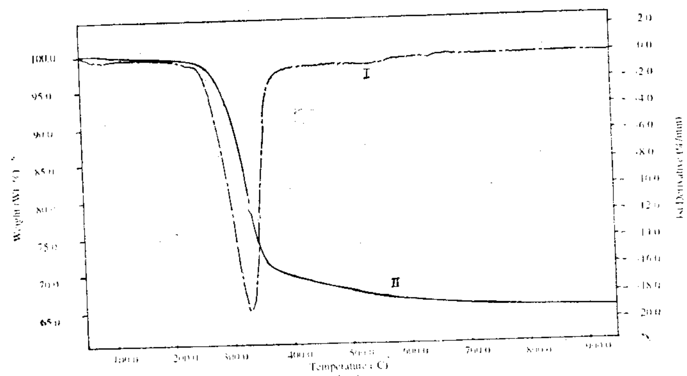

Fig 1

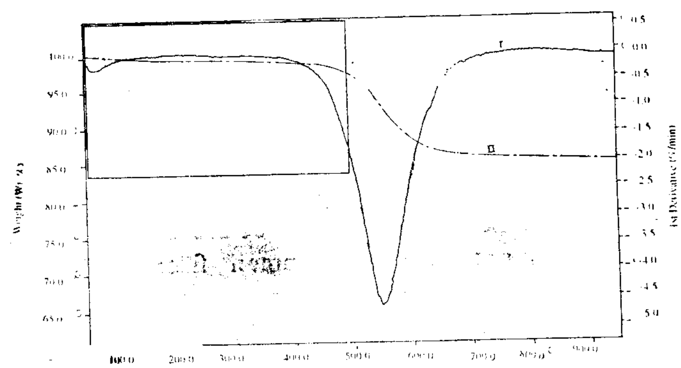

Fig 2

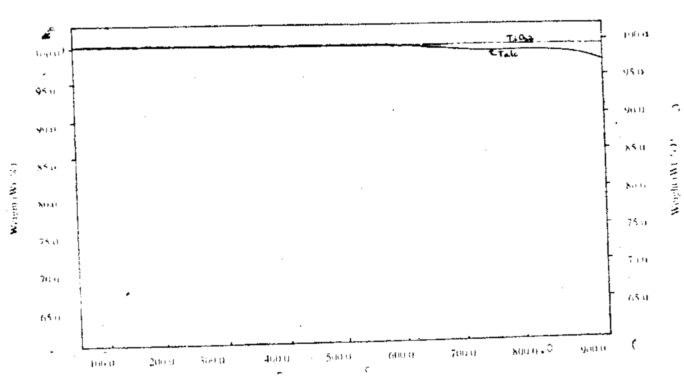

Fig 3

The DTG curve (Fig. 1–II) of alumina hydrate shows a clear peak at temperature of 327.5 °C. The weight loss commences at 230 °C and continues upto 540 °C. The thermogram of clay (Fig. 2) also indicates a sharp peak at 547.5 °C (II) with the range of weight loss from 435°C to 720°C (Table–1). On the other hand, the thermograms of titania and talc do not exhibit any peak for decomposition in the range of temperatures studied. However, it can be seen in Table–1 that the weight loss is initiated at 600°C in talc and from the beginning in titania very sluggishly continuing upto 940°C. The ash percentage at 940°C shows little loss in weight for titania (99.2%) and talc (97%) compared to clay (85.5%) and alumina hydrate (65%). The loss in weight of alumina hydrata has previously been explained (8) due to elimination of water molecules while in clay it is due to dehydroxylation (9).

The thermograms are quite valuable in deciding the temperature upto which the filler materials should be heat treated. As the temperature increares, the structural changes also take place resulting in alteration of texture of the materials, density, pore volume and hydrophillic characteristics. The heat treated products have direct repercussions on the strength properties of paper. The optical, sizing and printability properties are also affected considerably because of the heat treatment of the filler materials.

Bond factor :

Bond factor Vs temperature curves for eucalyptus and bamboo pulps having alumina hydrate and talc fillers are shown in Fig. 4. At 400°C, the bond factors with alumina hydrate increase considerably in case of eucalyptus and marginally in bamboo. At higher temperatures, bond factor decreases both in bamboo and eucalyptus. In the systems with talc, it remains unaltered, in bamboo at 400°C beyond which, it increases to some extent. In eucalyptus, there is a sharp decrease in bond factor value but it rises considerably at higher temperatures (600 and 800°C). The difference in variations of bond factor with temperature is due to the surface and structural transformations occuring in the two solids on heat treatment. At 400°C, surface area of alumina hydrate increases significantly. The reactions taking place with the two solids on thermal treatment are:

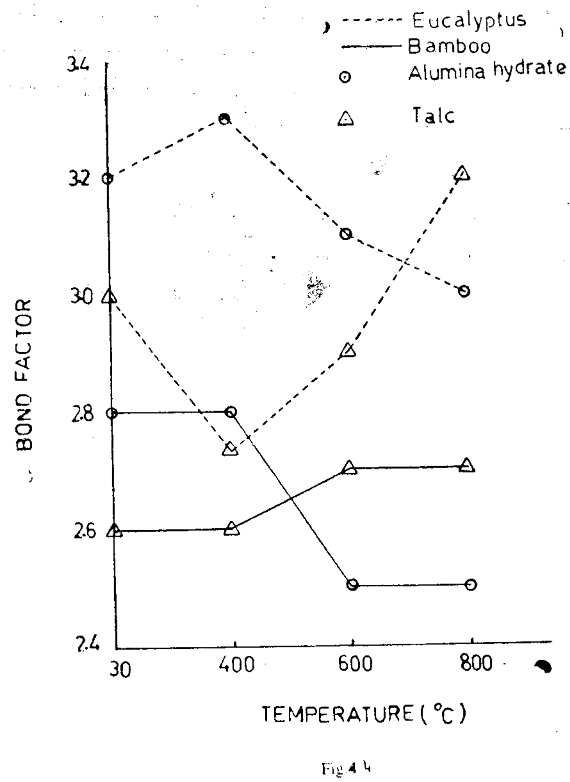

Fig. 4

$$Al(OH)_3 \cdot xH_2O \xrightarrow{120^\circ C} Al(OH)_3 \cdot 3H_2O \xrightarrow{400^\circ C} Al(OH)_3 \xrightarrow{800\text{–}1000^\circ C} Al_2O_3 \text{ and}$$

$$Mg_3(Si_2O_3)_2(OH)_2 \longrightarrow MgO.\ 4SiO_2H_2O \xrightarrow{600^\circ C}$$

$$MgO.\ 4SiO_2 \xrightarrow{800^\circ C} MgO \text{ and } SiO_2 \xrightarrow{1200^\circ C} Mg_2SiO_3$$

As the temperature is increased, the structural water in $Al(OH)_3$ is slowly eliminated with decrease in surface area and porosity. Consequently, the bond factor increases initially but decreases gradually above 400°C. On the other hand, in talc, the dehydroxylation reaction commences at 400°C, but progresses very sluggishly without serious structural disorganisation and therefore, the bond factor increases after 400°C.

Fibre strength factor :

Fibre strength factor of the hand sheets filled with thermal treated fillers have been shown in Fig 5. It can be seen that fibre strength factor gradually decreases with increasing temperature upto 600°C in both the fillers which drop significantly in paper having alumina hydrate treated at 800°C.

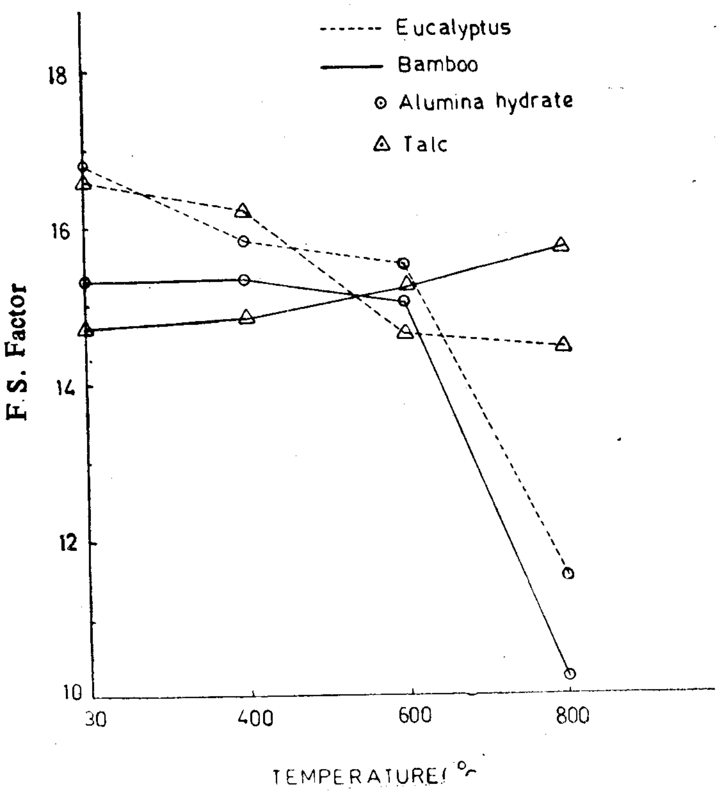

Fig. 5

Sizing of Paper:

Results on sizing of paper (thiocyanate flotation method) have been reported in Tables–2 to 8 The effect of increasing filler content on sizing in bamboo and eucalyptus pulp is shown in Table–2 and 3 respectively. It can be seen that there is an improvement in sizing of paper with increasing amount of both talc and alumina hydrate. However, in case of titania and clay it is the reverse. This is because of the highly fine powder nature of talc and alumina hydrate which are hydrophobic in character (10).

Sizing of paper in presence of cationic and neutral starch is also improved in both bamboo and eucalyptus pulp (Tables—4 and 5. As these starches are used for higher retention and strength improvement, the sizing property reported is of high significance. However, the thermal treatment of both the fillers affect the sizing property irrespective of the furnish excepting with mixed pulp having talc heated at 400°C (Tables—6 to 8). This may be due to increase in basic character of fillers occuring during dehydration. It effects the fibre-rosin adsorption phenomena and thereby sizing efficiency (11). Moreover, the surface area of solid increases on heat treatment which adsorbs water easily and thus sizing becomes poor. The highly porous nature of the paper sheets with heat treated fillers facilitates water penetration (12). Washburn equation can be examined to interpret the sizing properties of the two sets of paper.

According to washburn equation. penetration, of liquid through capillaries is governed by ;

$$l^2 = \frac{r.t\ \gamma \cos\theta}{2\eta}$$

Where l is depth of liquid penetration at time period, t in the capillary with pore radius r. The surface tension of the liquid is γ and viscosity is η The contact angle between the liquid and solid surface is θ.

With thermal treated alumina hydrate and talc, contact angle θ is reduced significantly (cos θ increases) because of the higher pore radius (r) and increased surface area of the filler due to heat treatment and consequently l increased and the internal sizing becomes poor. At higher filler loading or in superfilled paper, the total pore volume of the paper is reduced i. e., 'r' and therefore 'l' is reduced, bringing in better sizing i.e., the penetration resistance is enhanced.

Porosity :

Porosity of hand sheets made with bamboo, eucalyptus and mixed pulp with heat treated fillers are shown in Figs. 6 to 8. It can be seen that the sheet becomes porous with talc (600°C) in both bamboo and eucalyptus significantly and with alumina hydrate marginally. So this structural modification of fillers may find utility in the production of highly porous absorbent grades of paper and printing papers where porosity is a controlling parameter.

TABLE—1
TGA results of different fillers

Filler	T max (°C)	Weight loss (%) (Decomposition and Volatile)	Ash (%) at 940°C
Alumina hydrate	327.5	31.9 in between 230°C & 540°C	65.0
Clay	547.5	12 9 in between 435°C & 720°C	85.5
Talc	800.0	2 9 in between 600°C & 940°C	97.0
TiO_2	940.0	0.8 at 940°C	99.2

Note: Tmax is the temperature at which maximum decomposition occurs.

TABLE—2
Sizing (seconds) in bamboo pulp using different fillers

Filler	Filler addition (%)				
	0	10	30	50	60
Talc	15.8	13.6	21.3	25.1	37.4
Alumina hydrate	15.8	20.62	18.4	21.5	16.5
Clay	15.8	14.8	11.4	3.1	0.9
Titanium dioxide	15.8	13.7	16.5	7.0	5.3

TABLE—3
Sizing (seconds) in eucalyptus pulp using different fillers

Filles	Filler addition (%)				
	0	10	30	50	60
Talc	27.2	28.9	34.6	43.5	34.3
Alumina hydrate	27.2	33.9	33.3	37.6	34.6
Clay	27.2	24.6	13.0	12.1	2.1
Titanium dioxide	27.2	28.4	20.9	11.8	11.5

TABLE—4
Sizing (seconds) in the handsheets using talc and starch (0.5%) with bamboo pulp

Starch	Filler (Talc) addition (%)			
	10	30	50	60
Cationic starch	14.0	28.7	22.8	24.6
Neutral starch	17.6	18.4	25.7	33 2

TABLE—5
Sizing (seconds) in the handsheets using talc and starch (0.5%) with eucalyptus pulp

Starch	Filler (Talc) addition (%)			
	10	30	50	60
Cationic starch	36.9	37.5	48.6	63 5
Neutral starch	43.9	49.5	52.6	55.8

TABLE—6
Sizing (seconds) in bamboo using thermal treated talc and alumina hydrate
(Tested as per Tappi UM 429)

Filler	Thermal treatment (°C)			
	30	400	600	800
Talc	15.3	10.1	0	3.6
Alumina hydrate	2.95	0	0	0

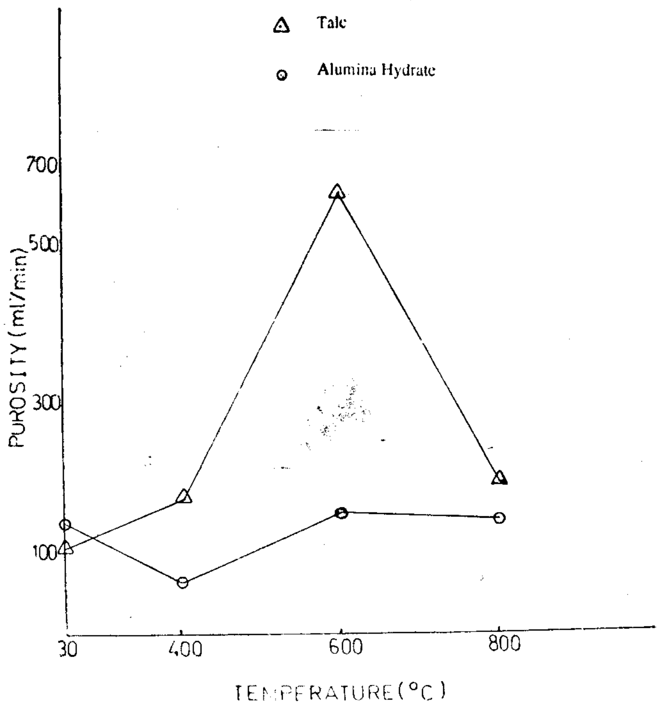

Fig 6

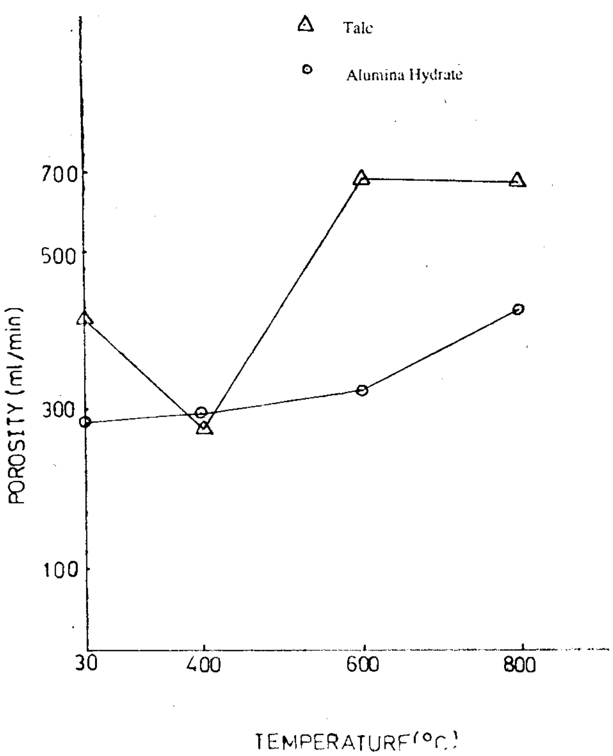

Fig.7

Printability :

Printability of the hand sheets in terms of ink density has been reported in Tables 9—12. It is observed from Table (9—11) that increase in filler content and incorporation of starch in the wet end improves printing properties (13). Surface ink gloss is better with alumina hydrate and titania followed by talc and clay. Printability of the paper is further improved by using thermal treated alumina hydrate and it increases proportionally with the temperature of heat treatment (Table 12). However, with heat treated talc, the trend is reverse. Ink gloss is lowered with increasing temperature,

The higher porosity existing in calcined filler based papers than the superfilled paper, is the main cause for better printability property in the former (14). Because of high porosity, the ink penetration becomes easier and the ink drying period is also shortened. Higher opacity and brightness observed in alumina hydrate after heat treatment, brings in better gloss values also. Thus paper with thermal treated alumina hydrate in particular can be superior to other types of fillers for printing purpose.

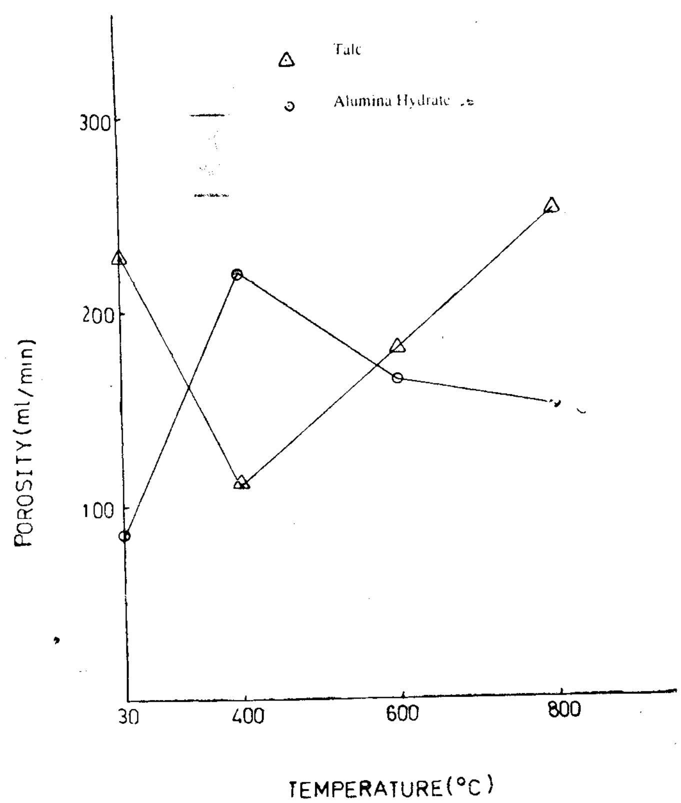

Fig.8

TABLE—7

Sizing (seconds) in eucalyptus using thermal treated talc and alumina hydrate (Tested as per Tappi UM 429)

Filler	Thermal treatment (°C)			
	30	400	600	800
Talc	4.1	4.6	1.6	0.9
Alumina hydrate	2.3	0	0	0

TABLE—8

Sizing (seconds in bamboo: eucalyptus (80:20) using thermal treated talc and alumina hydrate (Tested as per Tappi UM 429)

Filler	Thermal treatment (°C)			
	30	400	600	800
Talc	7.1	25.2	13.1	12.1
Alumina hydrate	2.6	0.2	0.3	0

TABLE—9

Printability of handsheets made with varying fillers in bamboo pulp

Filler	Filler dose (%)	Printability
—	—	65
Talc	10	68
Talc	30	70
Talc	50	72
Talc	60	75
Alumina hydrate	10	80
Alumina hydrate	30	83
Alumina hydrate	50	87
Alumina hydrate	60	90
Titanium dioxide	10	90
Titanium dioxide	30	88
Titanium dioxide	50	*82
Titanium dioxide	60	*80
Clay	10	60
Clay	30	63
Clay	50	66
Clay	60	70

*White dots visible

TABLE—10

Printability of handsheets made with varying fillers in eucalyptus pulp

Filler	Filler dose (%)	Printability
—	—	65
Talc	10	67
Talc	30	70
Talc	50	73
Talc	60	75
Alumina hydrate	10	80
Alumina hydrate	30	84
Alumina hydrate	50	87
Alumina hydrate	60	90
Titanium dioxide	10	90
Titanium dioxide	30	87
Titanium dioxide	50	*83
Titanium dioxide	60	*80
Clay	10	65
Clay	30	68
Clay	50	71
Clay	60	75

*White dots visible

TABLE—11

Printability of handsheets made with talc and starch in the wet-end

Furnish	Talc dose (%)	Starch (0.5%)	Printability
Bamboo	10	Cationic starch	70
Bamboo	30	"	75
Bamboo	50	"	78
Bamboo	60	"	80
Eucalyptus	10	"	75
Eucalyptus	30	"	78
Eucalyptus	50	"	83
Eucalyptus	60	"	85
Bamboo	10	Neutral starch	70
Bamboo	30	"	75
Bamboo	50	"	78
Bamboo	60	"	80
Eucalyptus	10	"	75
Eucalyptus	30	"	79
Eucalyptus	50	"	84
Eucalyptus	60	"	85

In lithographic printing process, all the properties studied here are important :

1 FS factor (strength of paper)

2 Bond factor (Interfibre bonding property)

3 Internal sizing

4 Porosity and

5 Printability.

FS factor is related to the breaking length and tearing strength properties. High tear and tensile strength are required to resist the stresses in operation on the press (15). It can be seen in Fig. 4 that the FS factor is quite appreciable for fillers, heated upto 600°C. While talc obtained at 800°C, can also resist to any deterioration in strength, alumina hydrate of 800°C can not be used as the FS factor is reduced substantially. The FS factor of 15–17 in these systems is comparatively inferior to 15–20 of paper (Fig 5) having ash content of 20% both for talc and alumina hydrate. However, paper with 28% alumina hydrate can also be suitable.

Bond factor, having rapport with the bursting strength, and porosity (16,17) counts for suitability of paper for printing purpose. The bond factor of paper having thermal treated fillers (upto 800°C) is higher than the superfilled paper (upto 28%) of filler with talc and alumina hydrate.

Internal sizing, gives measure of water penetration. Excepting, the mixed pulp, it is found (Tab e-6, 7) that the time of penetration is reduced even to zero in paper with thermal treated fillers. On the other hand, the sizing improves in papers at all levels of filler loading.

Conclusion :

The structural changes occuring in the filler material affect the overall property of paper. The bond factor as well as FS factor are improved or remain unaltered upto 400—600°C. At 800°C, the structural degradation takes place and these properties are found to get deteriorated.

TABLE—12
Printability of handsheets made with varying thermal treated fillers in the wet end

Furnish	Filler	Filler dose (%)	Thermal treatment of filler (°C)	Printability
Bamboo	Talc	20	400	60
Bamboo	,,	20	600	55
Bamboo	,,	20	800	50
Eucalyptus	,,	20	400	60
Eucalyptus	,,	20	600	55
Eucalyptus	,,	20	800	50
Bamboo : Eucalyptus (80:20)	,,	20	400	65
Bamboo : Eucalyptus (80:20)	,,	20	600	61
Bamboo : Eucalyptus	,,	20	800	55
Bamboo	Alumina hydrate	20	400	85
Bamboo	,, ,,	20	600	91
Bamboo	,, ,,	20	800	95
Eucalyptus	,, ,,	20	400	86
Eucalyptus	,, ,,	20	600	90
Eucalyptus	,, ,,	20	800	95
Bamboo : Eucalyptus (80:20)	,, ,,	20	400	85
Bamboo : Eucalyptus (80:20)	,, ,,	20	600	93
Bamboo : Eucalyptus	,, ,,	20	800	96

The internal sizing property of paper with heat treated fillers, is not enhanced, rather it decreases as the temperature is increased excepting incase of mixed pulp (Bamboo-hardwood) where it is found to improve. The internal sizing of paper is improved on increasing filler loading excepting in titania and clay. Printability of the paper is improved on using thermal treated alumina hydrate.

The air resistance values of the paper with heat treated filler materials are lower than paper having filler without heat treatment.

These modified fillers of alumina hydrate and talc can have applications in porous, fire retardant and absorbent papers.

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