Paper Quality Improvement Options and Effective Ways of Neutral/ Alkaline Sizing of Indigenous Pulps

Sood Y. V., Tyagi Sanjay, Pande P. C. & Roy T. K.

ABSTRACT

Most of the paper mills in India have switched over to neutral/alkaline sizing from conventional acidic sizing. The common problems being faced by them are slippage/improper cutting in the finishing section, creasing and rupture in printing press section and higher sizing chemical consumption as compared to the dosage being utilized for wood pulps abroad. The factors responsible for these drawbacks have been studied in detail. The possible ways of improving paper quality and sizing have been discussed.

INTRODUCTION

Amongst the paper properties, one of the important property for most grades of paper and paper board is the resistance to penetration by liquid. The paper intended for writing printing, wrapping, bags and various packaging and insulated boards are made resistant to liquid penetration and thus said to be "sized". Sizing is generally bought by sizing chemicals which provides the low energy coating to the fiber surface and must be able to form high contact angle with liquid in contact, in order to prevent the wetting of sheet of paper. In last two decades, Indian paper industry has gone through a phase of chemical evolution. Different new formulations of process and product additives have been introduced in the market and sizing chemicals is one of them (1-5). From the conventional acidic system with rosin paste and fortified rosin soap to neutral rosin dispersions, the industry has changed to neutral/ alkaline system with synthetic sizing chemicals like AKD and ASA. The driving force for this change is process advantage, product improvement and environmental considerations.

The change of sizing practice from acidic to neutral/alkaline type has given an option to papermakers to use Calcium Carbonate fillers in place of talc, the conventional filler presently being used by Indian paper Industry. Utilization of different fillers not only improves the process economics but also modifies the technical properties of paper like opacity, brightness, gloss, stability, smoothness, porosity and printability.

The Indian paper industry is highly fragmented and as such different varieties of raw materials viz. bamboo, hardwood, agricultural residues and waste paper are being used for papermaking

To identify the effective ways/ conditions of sizing, a detailed investigation was carried out for bamboo / hardwood pulp (20:80) and agricultural residues pulp using AKD sizing emulsion with different fillers viz. PCC, GCC and Talc.

RESULTS AND DISCUSSIONS

Bamboo and Hardwood Pulp

Sizing Response

All the GCC fillers, received from different sources, have shown good sizing with AKD ($Cobb_{60}$, 17 to 20 g/m^2; ***(Table II)***. However, there is wide variation in sizing response towards PCC of different origin ***(Table I)***. Out of four PCC samples, only two have given sizing response. One sample has shown sizing degree ($Cobb_{60}$) of 19.7 and the other 22.4; the remaining two samples have shown quite higher sizing values of 63.4 and 109.4. Considering the sizing definitions illustrated in (***Table III)***, PCC filled sheets had not shown

Table I : Sizing response of bamboo and hardwood pulp (20:80) with PCC collected from different sources under Neutral/alkaline conditions

Properties	Cobb values obtained for the samples containing PCC collected from different sources				
	Blank	1	2	3	4
Cobb 60 (g/m2)	17.7	22.4	63.4	109.4	19.7
Cobb 60 (after 1 week)	17.8	22.6	69.6	118.6	20.2
Cobb60 (after 3 weeks)	17.7	24.6	70.4	122.2	20.3

Table II: Sizing response of bamboo and hardwood pulp (20:80) with GCC collected from different sources under Neutral/alkaline conditions

Properties	Cobb values obtained for the samples containing GCC & Talc					
	1	2	3	4	5	Talc
Cobb 60 (g/m2)	20.4	18.9	16.9	16.6	16.8	14.6
Cobb 60 (after 1 week)	20.2	18.9	16.8	16.4	16.9	14.6
Cobb60 (after 3 weeks)	20.6	19.0	16.9	16.5	16.8	14.6

Table-III: Sizing definitions

When tested	Normal sizing	Poor sizing	Size reversion	Fugitive sizing
Off Machine	In specification	Out of specification	In specification	Out of specification
Oven cure	-do-	In specification	-do-	In specification
24 hours natural curing	-do-	Out of specification	-do-	-do-
1 week natural curing	-do-	-do-	Lower sizing	Lower sizing
3 week natural curing	-do-	-do-	Remains constant at lower level	No sizing

Central Pulp & Paper Research Institute, Saharanpur, 247001

fugitive sizing; however, slight size reversion was observed in the case of two samples and higher in the remaining two samples. The loss in sizing can be the result of hydrolysis of unreacted AKD into ketone or a slow cleavage of the ester bond occasioned by higher levels of alkaline material in the finished paper. GCC filled sheets have not shown any size reversion problem. The other cause may be porous structure of PCC than GCC due to which a large fraction of AKD is getting occluded within the pores of PCC.

Strength properties

(Table IV) shows the different strength, optical and surface properties of hardwood/bamboo pulp handsheets prepared using different types of fillers. Precipitated Calcium Carbonate filled sheets are more bulky, having lower apparent density than GCC filled sheets. The addition of filler adversely affects most strength properties by directly interfering with inter fiber bonding. Tensile strength, which mainly depends on the inter fiber bonding, is relatively more adversely affected by PCC than GCC . This is probably due to the presence of relatively finer particles in PCC than GCC. GCC has larger particle size and chunky shape and hence less detrimental to strength. Furthermore, the strength reduction is also due to stress concentrations in the sheet, originating from cracks and pores etc. Similarly the folding endurance of PCC filled sheets are lower than GCC filled sheets. The extent is different for GCC of different origin. The reduction in tensile stiffness in case of GCC is lesser than PCC, probably due to lower impact on sheet thickness and bulk in case of GCC than PCC. This is probably due to the reason that GCC has coarser particles than PCC. Finer filler PCC has lower tensile stiffness, than GCC. The tensile strength and tensile stiffness reduction is maximum in case of talc.

The effect on tearing strength is similar for both GCC and PCC. PCC filled sheets have slightly higher tearing strength. The development of tear strength depends on the degree of fiber bonding in a sheet. The tear strength is less sensitive to loading in a well-bonded sheet, because work needed to break well bonded fibers in unfilled fiber network is not much higher than pulling out the whole less bonded fibers from filled sheets. Generally in the paper made from a beaten chemical pulp furnish, where the fibers are well bonded, the introduction of filler not necessarily reduce the tear strength unless higher filler levels are reached.

Table IV: Strength, Optical, and Surface Properties of bamboo and hardwood pulp (20:80) with PCC, GCC & Talc as fillers .

Properties	Values obtained for the samples containing PCC, GCC & talc			
	Blank	PCC	GCC	Talc
Apparent Density(g/cm^3)	0.65	0.60	0.63	0.66
Porosity (ml/min.)	822	1760	1920	1790
Roughness, Bendtsen (ml/min)	429	303	400	219
Optical Properties				
Brightness (%)	80.5	87.6	84.9	82.3
Whiteness (%)	36.8	61.1	58.4	55.1
Yellowness (%)	17.4	10.4	10.6	11.0
Sp. Scattering Coefficient (m^2/kg)	32.4	53.5	48.1	40.2
Shade				
L*	92.26	94.98	94.44	93.42
a*	-1.04	-0.68	-0.80	-1.20
b*	9.52	5.82	5.89	6.20
Strength Properties				
Tensile Index (N.m/g)	45.0	29.0	30.0	25.5
Tensile Stiffness (MN.m/kg)	6.50	5.10	5.20	4.20
Tear Index ($mN.m^2/g$)	6.00	5.50	5.40	4.90
Burst Index ($kPa.m^2/g$)	2.10	1.45	1.15	1.20
Folding endurance (log_{10})	0.75	0.49	0.60	0.47
Ash (%)	0.7	15.2	18.3	18.1

Table V: Frictional Characteristics of bamboo and hardwood pulp (20:80) sized with AKD using Different Fillers.

	$Cobb_{60}$ (g/m^2)	Coefficient of Friction	
		Static	Kinetic
Pulp+0.6% AKD	20.2	0.248	0.231
Pulp+1% AKD	20.1	0.231	0.221
Pulp+2% AKD	20.0	0.207	0.198
Pulp+0.6% AKD+30% Talc	21.4	0.264	0.248
Pulp+0.6% AKD+30% GCC	22.2	0.328	0.313
Pulp+0.6% AKD+30% PCC	23.8	0.521	0.503

Optical properties

The PCC filled sheets have better optical characteristics than GCC & talc filled sheets. The PCC filled sheets have high specific scattering coefficient than GCC & talc filled sheet. This is due to finer particles in the former, which prevent the fibers from collapsing of fiber fines with fibrils. The filler generally prevent fibrillated areas of refined pulp from collapsing onto the fibers and helps in increasing the light scattering coefficient. To some extent, the interaction depends on the fiber type, fines content, and degree of beating as well as particle size of filler.

The improvement in brightness with the usage of PCC is 7 points as compared to 4 points for GCC. This is 2 points in the case of talc (***Tables IV***). The whiteness improvement is 24.8 points in PCC as compared to 21.6 points in case of GCC. This is only 18.3 in the case of talc. The yellowness reduction is relatively more in PCC. Talc filled sheets have relatively more greenish yellow shade as compared to PCC & GCC filled sheets, as indicated by higher a* and +b* color coordinates. Obviously this is due to the optical

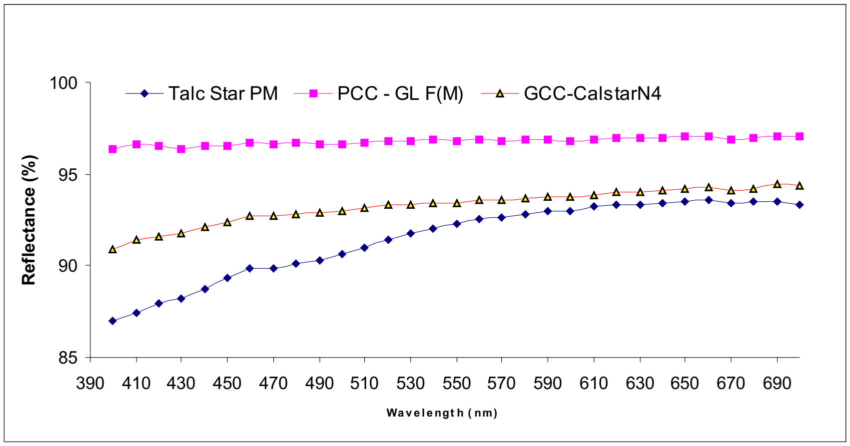

Fig1: Reflectance Curve for PCC, GCC and Talc

Table VI: Fracture toughness of bamboo and hardwood pulp (20:80) sized with AKD using Different Fillers

	Ash content	Fracture Toughness Index (mJ.m/g)
Pulp+0.6% AKD	0.8	8.32
Pulp+1% AKD	0.8	7.64
Pulp+2% AKD	0.8	7.26
Pulp+0.6% AKD+30% Talc	22.8	4.77
Pulp+0.6% AKD+30% GCC	22.6	7.40
Pulp+0.6% AKD+30% PCC	23.1	5.70

Table VII: **Contact angle of paper made from bamboo and hardwood pulp (20:80) using different fillers**.

Filler	Contact angle (?) after time interval (s)		
	1	10	Difference
Talc	125.9	125.2	0.7
GCC	127.5	126.7	0.8
PCC	117.8	116.2	1.6

Table VIII : Effect of different retention aids on filler retention, in furnish of agricultural residues.

Retention aid	Chemical Component	Particle charge Density(µeq/g)	Ash content (%)		
			GCC	PCC	Talc
Cationic Starch		+300	21.2	20.2	22.0
A (Imp)	Modified polyethylene imine	+1200	25.5	27.1	26.1
B (Imp)	Polyacrylamide	+2000	25.3	26.2	25.5
C (Imp)	Polyacrylamide	+1225	24.7	25.7	24.8
D (India)	Not known	+620	21.2	21.6	22.6

characteristics of filler. Fillers collected from different sources have different brightness & whiteness. The reflectance curve of talc, PCC & GCC is shown in Fig 1. PCC has flat reflectance at all wave lengths than other two fillers.

Retention of filler in neutral/ alkaline sized papers

In the presence of cationic starch but without any retention aid, the retention of GCC is about 3% more than PCC as indicated by higher ash content (***Table IV***). The retention of talc comes in between PCC and GCC.

Surface properties

The surface properties of paper are of utmost important in coating and in printing processes. The GCC filled sheets are more porous than PCC and Talc, probably due to coarse size in the former. Also PCC filled sheets are smoother than GCC filled sheets. Smoothness is best in case of talc as filler (***Table IV***).

Frictional Properties

There are several reports in the literature related to the importance of frictional properties of sheets and the reduction of friction parameter when AKD is used as sizing agent [6-11]. One of the problems being faced by Indian paper mills, who has switched over to AKD sizing is slippage in cutters in the finishing house. This problem was not experienced when sizing was carried out with rosin size and talc as filler. Even some paper mills manufacturing photocopier are facing relatively poor runnability problem in the photocopier machine, on switching over to AKD sizing with Talc as filler.

The frictional characteristics of pulp sized using dispersed rosin and AKD with different fillers were evaluated (***Table V***). Quite clearly excessive dose of AKD are showing negative effect on both static and kinetic friction, whereas not much positive effect is observed on cobb value with increase in dose. Handsheets prepared using different fillers indicated that PCC filled sheets have highest frictional parameters. This indicated that frictional related problems can be overcome using PCC or GCC as filler in conjunction with talc

Effect on Fracture Toughness

Creasing and rupturing of paper in printing press is primarily due to frictional property and fracture toughness (in line tear). The ability of paper to resist cracking while under tensile load is important for printing paper grades; runnability in the paper machine and in the printing press is partly attributed to the ability of the paper to tolerate flaws and defects. Fracture toughness of pulp sized using different dosages of AKD and different fillers were evaluated (***Table VI***). Clearly excessive dosage of AKD has negative effect on fracture toughness index. Presence of filler is reducing the fracture toughness and the negative effect is in the order: Talc>PCC>GCC. This indicated that substitution of talc with calcium carbonate fillers in AKD sizing can help in controlling the creasing problem in paper mills.

The property of a liquid to adhere to or wet a sheeted surface or to be absorbed

Table IX: Effect on Cobb and strength characteristics of agro residues pulp with PCC as filler.

Retention aid	Cobb (g/m^2)	Tensile index (N.m/g)	Tear Index (mN.m^2/g)	Burst Index (kPa.m^2/g)
Cationic starch	22.6	25.4	3.00	1.30
A (Imp)	19.0	27.5	3.10	1.40
B (Imp)	19.2	27.0	3.05	1.35
C (Imp)	19.6	26.5	3.05	1.35
D (India)	22.4	25.0	2.95	1.25

Table X: Effect on Cobb and strength characteristics of agro residues pulp with GCC as filler.

Retention aid	Cobb (g/m^2)	Tensile index (N.m/g)	Tear Index (mN.m2/g)	Burst Index (kPa.m^2/g)
Cationic starch	21.2	26.5	3.05	1.40
A (Imp)	18.7	29.5	3.20	1.50
B (Imp)	19.0	28.5	3.10	1.45
C (Imp)	19.0	28.0	3.10	1.45
A (India)	22.2	25.5	2.95	1.30

Table XI: Wetting rate of sheets made using different fillers and sizing chemicals

Dosages and chemicals (sizing chemicals and Fillers)	Time intervals (μs)		Wetting rate
	1.0	10	
Pulp+2.0%Dispersed rosin+2.5%PAC	117.5	112.1	0.60
Pulp+2.0%Dispersed rosin+ 30%Talc+2.5%PAC	118.8	114.7	0.46
Pulp+0.6%AKD	121	120.7	0.03
Pulp+1.0%AKD	127.9	127.7	0.02
Pulp+2.0%AKD	119.8	119.7	0.01
Pulp+0.6%AKD +30%Talc	127.8	125.1	0.30
Pulp+0.6%AKD +30%GCC	126.5	122.3	0.47
Pulp+0.6%AKD +30%PCC	125.0	121.3	0.41

by the surface or both is important in many aspects of paper manufacturing and converting as well as the end use applications of many converted paper products. This is well evaluated by contact angle measurements. The contact angle above 90 is generally better for water-based inks. The contact angle measurements were carried out using automated Fibro Contact Angle Tester for sheets having talc, GCC, and PCC as fillers. The results are recorded in ***Table VII***. All the fillers with AKD sizing agent showed contact angle of more than 110. The change in contact angle with time is relatively higher in the case of PCC as filler than talc and GCC. This indicates that substitution of PCC in talc will avoid break in flow of ink onto paper, which is a general problem, observed with AKD usage as sizing agent.

Agricultural residue pulps

Agricultural residues pulps are characterized by poor strength properties, low drainage on wire part, poor surface properties, increased fluff generation on paper machine and higher consumption of chemicals. Due to this making of neutral/alkaline sized paper from agricultural residues with addition of fillers is a typical task. A detail investigation was carried out in present work regarding sizing response, strength and optical characteristics of neutral/alkaline sized paper made from agricultural residue pulps.

Sizing Response and Retention of fillers

In the presence of cationic starch but without any retention aid, the retention of GCC is about 1% more than PCC and talc has maximum retention. Different commercial retention aids available were tried. The dosage used in all the cases was 0.02%. It can be seen that the retention of fillers can be improved by using different retention aids. ***(Table VIII)***

The effect on Cobb value and strength characteristics with the usage of different retention aids is given in (***Tables IX, X)***. Usage of proper retention has shown improvement in Cobb and marginal improvement in paper characteristics viz tensile index, tear index and bursting strength.

Contact Angle of Paper Sized with Dispersed Rosin and AKD and their Effect on Printing Characteristics

The contact angle between air, liquid and paper or board is more appropriate in assessing the wetting or hydrophobicity of the paper than cobb test. In this a small drop of water is placed on the paper surface and the contact angle is measured with the aid of high-speed camera. The contact angle for papers sized with dispersed rosin and AKD sizing emulsion with different fillers are given in ***Table XI***. The wetting rate was calculated by using the following formula:

$$\textbf{Wetting Rate} = \frac{c_{1.0} - c_{10}}{t_2 - t_1}$$

Where $c_{1.0}$, is contact angle at time interval of 1.0 μs .

c_{10}, is contact angle at time interval of 10 μs.

t_2 and t_1 are time rates which are 10 and 1.0 μs respectively.

The wetting rate indicated that with the usage of AKD instead of dispersed rosin at neutral pH the wetting rate got reduced appreciably (0.6 to 0.03). Excessive usage of AKD emulsion reduces the wetting rate adversely. Use of talc along with AKD, which is the present practice in Indian paper mills, gave lower wetting rate than GCC and PCC. This is probably due to high surface energy of talc (42.9mJ/m^2). The print density values obtained for different handsheets after printing on the IGT printability tester are given in ***Table XII.*** Clearly GCC and PCC filled sheets have higher print density than talc with AKD sizing. Keeping this in view, it is recommended that paper mills should replace talc partly with PCC or GCC.

Table XII: Print Density of Papers sized with Dispersed Rosin and AKD using Different Fillers.

Handsheets	Print Density (McBath)
Dispersed Rosin + PAC + Talc	1.15
AKD+Talc	0.92
AKD + GCC	1.2
AKD+PCC	1.22

Table XIII: Strength, Optical, and Surface Properties of agricultural residues pulp with PCC, GCC & Talc as filler

Properties	Values obtained for the Samples			
	Blank	PCC	GCC	TALC
Apparent Density(g/cm^3)	0.78	0.66	0.70	0.77
Porosity (ml/min.)	155	602	730	241
$Cobb_{60}$ (g/m^2)	21.8	25.6	23.8	19.0
Roughness, Bendtsen (ml/min.)	350	166	180	163
Optical Properties				
Brightness (%)	77.1	83.9	82.2	82.1
Whiteness (%)	45.2	66.2	50.2	52.7
Yellowness (%)	14.0	10.3	13.0	11.0
Sp. Scattering Coefficient (m^2/kg)	43.0	54.7	49.5	46.8
Shade				
L*	90.6	92.6	91.4	91.3
a*	˜ 0.60	˜ 0.56	-0.59	-0.91
b*	7.37	5.53	6.90	5.92
Strength Properties				
Tensile Index (N.m/g)	43.0	27.5	29.0	26.0
Tensile Stiffness (MN.m/kg)	5.90	4.30	4.70	4.13
Tear Index (mN.m^2/g)	4.05	3.30	3.20	3.00
Burst Index (kPa.m^2/g)	2.10	1.30	1.40	1.25
Folding endurance (log_{10})	1.20	0.57	0.62	0.55
Ash (%)	4.40	20.2	21.2	22.0

Table XIV : Frictional Characteristics of Agricultural residues pulp Sized with AKD using different fillers

Dosages of AKD and Fillers	$Cobb_{60}$ (g/m^2)	Coefficient of Friction	
		Static	Kinetic
Pulp+0.6% AKD	21.2	0.28	0.27
Pulp+1% AKD	21.3	0.26	0.25
Pulp+2% AKD	21.3	0.22	0.21
Pulp+0.6% AKD+30% Talc	22.3	0.32	0.30
Pulp+0.6% AKD+30% GCC	22.4	0.38	0.35
Pulp+0.6% AKD+30% PCC	22.8	0.60	0.51

Strength properties

Precipitated calcium carbonate filled sheets are more bulky than GCC and talc filled sheets (**Table XIII**). Tensile strength, which mainly depends on the inter fiber bonding, is relatively more adversely affected by PCC than GCC. Talc showed maximum reduction. Similar is the trend in folding endurance. The reduction on tensile stiffness in case of GCC is lesser than PCC and talc, which is probably due to finer filler particles in PCC than GCC. PCC filled sheets have slightly higher tearing strength than GCC- as well as talc-filled sheets.

Optical Properties

The PCC filled sheets have better optical characteristics than GCC filled sheets (***Tables XIII***). The PCC filled sheets have 5.2 m^2/kg higher specific scattering coefficient than GCC filled sheets and 7.9 m^2/kg higher Sp. Sc. Coefficient than talc filled sheets. This is probably due to finer particles in the former, which prevent the fibres from collapsing of fibre fines and fibrils. The improvement in brightness with the usage of PCC is above 6.8 points, compared to 5 points for GCC and talc. The whiteness improvement is 21 points in PCC and about 1517 points in the case of GCC. The yellowness reduction is relatively more in PCC. GCC filled sheets have relatively darker shade as compared to PCC, which is indicated by higher a* and b* colour coordinates.

Surface properties

The surface smoothness of sheets is better in case of PCC than GCC as filler. Talc filled sheets were found to be best in smoothness. GCC filled sheets have higher porosity than PCC and talc filled sheets (***Tables XIII)***.

Frictional Properties and Fracture Toughness

Effect of frictional properties and fracture toughness on agricultural residues pulps using different fillers was evaluated (***Tables XIV & XV***). Similar trend was observed as observed in case of bamboo and hardwood pulps (20:80). Excessive dosage of AKD gave negative effect on frictional characteristics. PCC filled sheets have higher frictional coefficient followed by GCC and Talc. Fracture toughness is best in case of GCC filled sheets.

Effect of different fillers on Contact angle

The property of a liquid to adhere to or wet a sheeted surface or to be absorbed by the surface or both is important in many aspects of paper manufacturing and converting as well as the end use applications of many converted paper products. This is well evaluated by contact angle measurements. The

Table XV: Fracture toughness of Agro-residues pulp Sized with AKD using different fillers.

	Ash content	Fracture Toughness Index (mJ.m/g)
Pulp+0.6% AKD	1.3	5.90
Pulp+1% AKD	1.3	4.90
Pulp+2% AKD	1.3	4.80
Pulp+0.6% AKD+30% Talc	23.8	3.70
Pulp+0.6% AKD+30% GCC	23.7	5.10
Pulp+0.6% AKD+30% PCC	23.9	4.40

Table XVI : Contact angle of paper made from agro residues pulp using different fillers.

Filler	Contact angles (in Degree) after time interval (in sec.)		
	1	10	Difference
Talc	119.6	118.6	1
GCC	121	119.9	1.1
PCC	116.7	114.8	1.9

contact angle above 90 is generally better for water-based inks. The contact angle measurements were carried out using automated Fibro Contact Angle Tester for sheets having talc, GCC, and PCC as fillers. The results are recorded in ***Table XVI***. All the fillers with AKD sizing agent showed contact angle of more than 110. The change in contact angle with time is relatively higher in the case of PCC as filler than talc and GCC. This indicates that substitution of PCC in talc will avoid break in flow of ink onto paper, which is a general problem, observed with AKD usage as sizing agent.

CONTROLLING OF SIZING PROBLEMS OCCURRING WHILE USING CARBONATE FILLERS

The problems generally observed in Neutral sizing with the usage of carbonates as fillers are-

- Sizing reversion
- Fugitive sizing
- Higher consumption of sizing chemicals

Sizing reversion is basically a decrease in fluid resistance over time, as paper is stored or shipped. The effect can be observed occasionally in most kind of sized papers but most commonly observed in Neutral sizing, when carbonate fillers are used along with AKD as sizing chemical.

Fugitive sizing effect is observed when paper has cobb value out of specification, off machine but comes in specified range on oven curing and natural curing for 24 hours. Afterwards sizing gets lower and no sizing is observed after 3 weeks.

Factors those are likely to cause variability of sizing are some of the same factors that can cause shift in retention efficiency and other changes in wet end. One needs to find out whether changes in water resistance in paper or in the demand of sizing agent can be correlated to other cycles in the system. Some times, increased level of surface active material that act as anti sizing agents, may be a cause of loss or reduction in sizing. Such materials may include black liquor carry-over, components of coated broke formulations, and non ionic surfactants from deinking operations, component of dye formulations or slimicide formulations, and various anti-foam surfactants.

These problems become more predominant, if the sizing chemicals are not used optimally. These problems discourage the papermaker to switch over to carbonate fillers from the conventional filler Talc. However certain process conditions and system variables, if manipulated properly, can reduce the problem.
The following two steps were tried to improve the sizing with AKD using calcium carbonate as filler:

- Partial substitution of calcium carbonate with talc
- Improving the filler retention

Partial Substitution of Calcium Carbonate with Talc

To reduce the problems associated with neutral sizing using PCC, it is suggested to move forward for using filler blends i.e. to use combinations with Talc instead of using carbonate fillers alone. It has been observed that neutral sizing if carried out with PCC or GCC alone, a number of problems occur, which may lead to adverse effect on product quality and hence contribute to the reduction in cost of the product and may lead to discouragement for the papermaker.

But an optimum substitution of Talc with PCC / GCC not only reduces problems of reverse and fugitive sizing but also shows good results in cost benefit analysis. Further it is believed that though PCC helps in improving optical characteristics of paper but at the same time, it lowers down the strength properties.

PCC particles having certain crystal shape like scalenohedral or rhombohedral structure, interferes more adversely in fiber to fiber bonding than those of platy Talc particles.

Hence partial replacement of carbonate fillers with Talc is beneficial from an overall point of view.

Causes of variation in consumption of sizing chemicals

The amount of consumption of sizing chemical varies from mill to mill. Actually there are some factors which are responsible for this fact**.** It has been observed that consumption of AKD sizing chemical in different mills varies widely. The general dose being used in Indian mills is in the range 1.2-1.5% in wood based mills; whereas it is 1.5-2.0% for agricultural residues based mills. The following conditions are needed to be considered for sizing optimization:

- pH
- Alkalinity
- Presence of alum
- Type and amount of filler particles present
- First pass retention level in the machine
- Colloidal nature of fibers
- Air content in the pulp

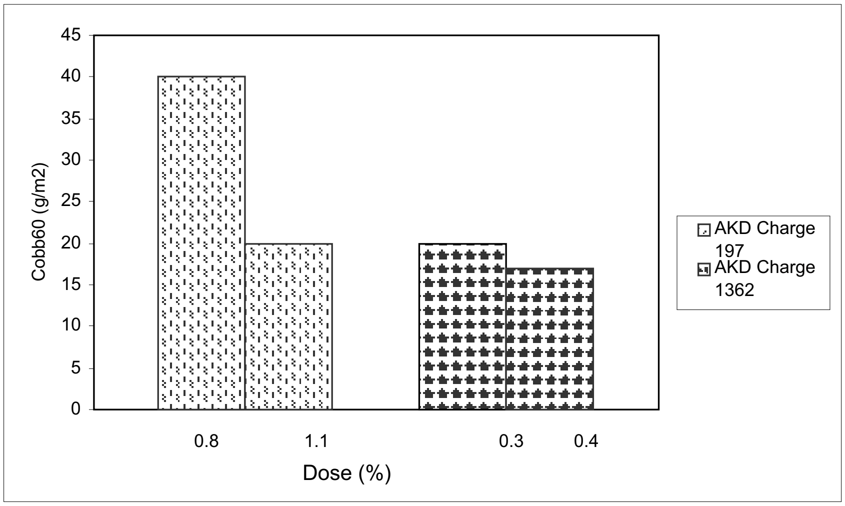

Fig. 2: Effect of AKD type on sizing of agricultural residues pulp **.**

Table XVII: Zeta potential of pulps collected from different mills.

Mill	Pulp	Zeta Potential (mV)
1.	Bamboo, CEpHED	-42.9
2.	Bamboo, C/DEPH	-39.9
3.	Hardwood, CEpHH	-39.2
4.	Hardwood, CpDEPD	-33.4
5.	Hardwood, C/DEOPDD	-43.5
6.	Hardwood, foreign origin	-32.5
7.	Softwood, foreign origin	-31.4
8.	Mixed agricultural residues, CEHH	-36.5
9.	Wheat straw, CEHH	-32.5
10.	Bagasse, CEHH	-38.5

Table XVIII : Amount of air in different pulps

Pulp	Air Content (%)
Softwood pulp	1–2
Hardwood pulp	2–3
Bamboo pulp	4–5
Straws, Bagasse	6–7

Effect of different parameters on sizing

pH

Although AKD is generally thought of as neutral and alkaline sizing agent, AKD is generally considered to be effective over a pH range of 6-9. The experiment conducted have shown that it is effective in the range of 7.5-8.0. Below pH 6 it ceases to be effective as sizing agent. Most probably it is likely that the lactone ring of AKD molecule ceases to be reactive with cellulosic hydroxyl groups. Below this pH value no permanent sizing is achieved.

Alkalinity

The presence of bicarbonate ion alkalinity is absolutely essential to be able to function as an internal sizing agent [12, 13]. Normally 150-250 mg per kg expressed as $CaCO_3$ is considered optimum. Addition of carbonate filler either PCC or GCC helps in attaining better effectiveness of AKD size.

Alum

Aluminium sulphate or paper maker's alum presence is detrimental to produce acceptable performance for AKD sizing chemical. This is probably due to prevention of beta-keto ester bond or changing orientation of sizing molecule [13].

Fillers and Fines

Fillers affect the performance of AKD sizing. The amounts of size preferentially adsorb by the filler particles over either fiber or fines affect the sizing efficiency, since the sizing compound on the filler surface cannot contribute to a substantial way to make the sheet the hydrophobic. If the furnish has significant amount of fines present more than 5%, which is always higher in the case of Indian paper mills, first pass retention is a critical parameter.

Colloidal nature of fibers

In papermaking there is extremely unfavorable conditions as there is very high dilution level, fiber concentration is less than 1% along with strong turbulence and high shear forces, which allow short contact with fibers. To make sizing effective it becomes necessary that colloidal zeta potential of the fibers are examined. Indian paper mills there are wide diversity of fibrous raw materials being used and the bleaching mode varies from mill to mill. Different pulp samples collected from different mills were examined using Mutek zeta potential instrument. There is wide variation in the Zeta potential values of pulps obtained from different mills. All the pulps have higher negative Zeta potential than imported pulps (***Table XVII***).AKD emulsions normally available in the international market are with different charge densities, i.e., low, medium, and high. The average particle size in these dispersions are 1-5 µm with pH range 2-4. AKD emulsions used in the present study were procured from the renowned suppliers in India. The particle size in these emulsions were found to be in the range 1 to 2 µm and the particle charge was 50-197 µeq/g, i.e., low to medium charge density. For these emulsions the required dosage to get Cobb value around 20 g/m^2 was found to be in the range 0.7 to 0.8% for bamboo and hardwood pulp and 1% to 1.1% for agricultural residue pulp. These dosages are quite higher than the dosage generally reported (0.1% to 0.3%) in the literature for wood pulp. The zeta potential for pulps collected from different mills indicated that these pulps have relatively higher negative charge than pulps of foreign origin.

Table XIX : **Effect of air on the characteristics of Bagasse pulp.**

Properties	Values obtained		
	1	2	3
App Density (g/cm^3)	0.7	0.68	0.71
Tensile index (Nm/g)	29.5	26.0	31.5
Burst index (kPam^2/g)	1.65	1.50	1.80
Tear index (mNm^2/g)	3.50	3.40	3.65
Porosity (ml/min)	510	550	490
Sp. Sc. Coefficient (m^2/kg)	32.3	31.2	39.5
Cobb60 (g/m^2)	21.5	25.5	20.5

Table XX: **Effect of air on the characteristics of bamboo and hardwood pulp (20:80).**

Properties	Values obtained		
	1	2	3
App Density (g/cm^3)	0.68	0.66	0.69
Tensile index (Nm/g)	40.5	37.0	42.5
Burst index (kPam^2/g)	1.85	1.70	1.95
Tear index (mNm^2/g)	4.85	4.65	5.05
Porosity (ml/min)	740	810	720
Sp. Sc. Coefficient (m^2/kg)	46.7	43.8	45.8
Cobb60 (g/m^2)	20.5	24.5	19

Note: 1-as such; 2-with air; 3-with antifoam

Keeping this in view, AKD emulsion of high charge density was procured from a foreign source and was tried. This AKD emulsion had AKD particle size in the same range that was observed for indigenous samples but the particle charge was quite high, i.e., 1360 µeq/g. Using this AKD emulsion it was observed that satisfactory sizing ($Cobb_{60}$, 20 g/m^2) can be attained using 0.3% dosage which is about 1/3rd of the dosage normally being used for agricultural residues (**Fig. 2**). Similarly bamboo and hardwood pulp blends could be sized using 0.2% AKD emulsion.

Air Content in Pulp

Entrained air in the pulp affects the paper quality and paper properties [14-16]. A pulp suspension apart from water and fibers also contain air and other gaseous components. Gases do not usually disturb mechanical processes or flow behaviour, but they may cause detrimental in bleaching and biological activity. Gases in bubble form may disturb both mechanical and chemical operations. The air content in different types of pulp was measured using Techpap Air tester and it was observed that its amount is different in different pulps and the observations are recorded in ***Table XVIII.***

From the table it is clear that straws and bagasse have tendency to contain more air as compared to other pulp types.
To estimate the effect of air on the sizing and other characteristics, the handsheets were prepared with pulp as such and with pulp in which additional air was introduced` and sizing was done with AKD. Results are recorded in the table ***Table XIX & XX***.

The results indicated that the characteristics like tensile index, burst index, tear index, specific scattering coefficient adversely affected by the presence of air. The porosity is positively affected. Removal of air can help in attaining better characteristics including sizing.

CONCLUSIONS

- AKD size is more effective in the pH range 7.5-8.0, in presence of carbonate fillers. Presence of Alum gives detrimental effects in AKD sizing.
- Pulp samples collected from Indian paper mills has relatively higher negative Zeta Potential as compared to pulps of foreign origin.
- AKD emulsions being presently used by Indian paper mill have low to medium charge density ranging 50-197 µeq / g. The dosages of AKD used by Indian paper mills in sizing can be reduced by using emulsion of higher charge density.
- Air content (in bubble form) in agro residues pulps is relatively higher than other type of pulps. Steps to control air content in pulp will help in reduce the dosages of AKD size emulsion in sizing with agro residues pulps.
- Wetting rate measured by contact angle is lesser in case of AKD emulsion than dispersed rosin. Excessive dose of AKD offers this property adversely.
- The change in contact angle with time is relatively higher in case of PCC which indicated that its substitution with Talc will help in overcoming the problem of break in flow of ink onto the paper.

EXPERIMENTAL

Bleached pulp sample containing 80% hardwood pulp and 20% bamboo pulp, which is a typical, furnish of large sized paper mills in India, and agricultural residue pulp was collected from mills for the study. The pulp was beaten in PFI mill to freeness level of 350±50 ml as per ISO 5264/2-1979 (E) method. All the chemicals viz. AKD, retention aids, cationic starch and fillers viz. Talc, PCC and GCC were collected from the different commercial manufacturers and suppliers. The sizing of pulp was carried out with 0.8% AKD emulsion, at a pH of (8-8.5) along with different retention aids at a dosage level of 0.02% on O.D. pulp basis. Hand sheets were prepared on Rapid Kothen sheet former having backwater recirculation system, according to ISO 5269/2 method. These sheets were conditioned (Temperature 27±1^{0}C, Relative humidity 65±2% specified for tropical countries under ISO: 187-1990) prior to testing. The following tests were carried out as per standard methods: (i) Thickness, ISO 534:1988 (E); (ii) Tensile strength, ISO 1924-2:1994 (E); (iii) Tear strength, ISO 1974:1994 (E); (iv) Bursting strength, ISO 2758; (v) Specific scattering coefficient, SCAN C 27-69; (vi) Folding endurance, ISO 5626:1993 (E); $Cobb_{60}$, ISO 535; (vii) Contact angle, using Fibro Dynamic Contact Angle Tester.

REFERENCES

1. Roberts J. Neutral Sizing PIRA Review of Pulp and Paper Technology. PIRA International. Leatherhead, Survey, U.K.

2. Rohringer P; Bernheim M; Wertherman P D. Are so called reactive sizes really cellulose reactive. Tappi, J 68 (1), 83, 1995.

3. Isogai A. Mechanism of paper sizing by Alkyl Ketene Dimer. J. Pulp Pap. Sci. 25 (7) 251, 1999.

4. Hodgson K T. A review of paper sizing using alkyl ketene dimer versus alkenyl succinic anhydride. Appita J, 47 (5), 402, 1994.

5. Dumas D H. An overview of cellulose reactive sizes. Tappi J, 64 (1), 43, 1981.

6. Arif Karademir, Dick Kholyand, Nicholas Wiseman and Huining Xiao, A study of the effects of alkyl ketene dimmer and ketone on paper sizing and friction properties, Appita J., Vol. 57, No. 2 (2004).

7. Hoyland, R.W., and Neil, M. Factors affecting the frictional properties of paper-the effect of AKD neutral size, Pap Technol. 42(3):45(2001).

8. Back, E.L. Paper to paper and metal to metal friction, Proc. Intl. Paper Physics Conference, Tappi Press, P. 49 (1991).

9. Inoue, M. Gurnagul, N. and Aroca, P. Static friction properties of linear board, Tappi J. 73(12):81 (1990).

10. Daul, M. The influence of deinked fibre to winding of newsprint rolls, Newsprint forum, Atlanta, USA, p.53 (1992).

11. Beatty, J. To slip or not to slip? An answer to the question, Papermaker 57(4):31(1994).

12. Lindstorm, T., and Sodeburg, G., Nordic Pulp & Paper Res J. 2, 3945 (1986).

13. Kevin, T., Hodgson, A review of paper sizing using AKD vs. ASA, Appita, Vol. 47, No. 5.

14. Topi Matti Helle, Paperija Puu Paper and Timber, Vol. 82 /No.7/ 2000, p-457

15. Tapio Pietikäinen, on- line air entrainment tests on paper machine, Tappi Journal (November 1992) p-185.

16. Tuomas Stoor, Rauli Virkkala , Olli Dahr and Jouko Niinimaki ,Apitta Journal, Vol. 53, No. 5, p-350.