

A Case Study on Alkaline Sizing in Agro-Based Paper Manufacturing

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ABSTRACT

Pulp and paper industry has been considered as vital and core industry and its *per capita* consumption has been used as an index of a country's development. Therefore, increase in *per capita* consumption can be taken as a growth in areas related to industrial, cultural and educational developments. India has a great paper market because of large population and we have to still import large quantity of writing & printing grade of paper. It has been observed that the consumption of higher brightness paper with more permanency is having very fast growth in printing industries. So it has become essential to adopt alkaline sizing to achieve the quality product goal. In this context numbers of trials were conducted in laboratory as well as in plant for successful establishment of AKD sizing in NTL, resulting brightness and permanency of paper achieved up to satisfactory level.

ABOUT THE MILL

The Naini Group of industries was established in the year 1998 with an initial production capacity of 50TPD of Kraft Paper. The campus is situated on Kashipur- Moradabad road at 7th K.M. from Kashipur. The capacity of the plant was increase to 65 TPD in the 2001 to produce Kraft and absorbent paper. A writing and printing grade of paper plant, Naini Tissues Limited was commissioned in May 2005 with the production capacity of 100TPD. Plant achieved its full production capacity with in a record time of eight months and is well known in market for its services and quality of product.

The main raw material is bagasse but to compensate the deficiency of bagasse, we are also using wheat straw approximately 50% off season. The mill have efficient wet washing system, continuous cooking, 4-stage brown stock washing system, 4-stage conventional bleaching sequence, continuous chemicals addition in stock preparation. The paper machine have the latest features like Mesto head box, Suction couch & pickup rolls, six number turning rolls uni-run, silent drive etc. The mill is planning to install oxygen delignification (ODL) plant in very near future.

INTRODUCTION

Paper sizing with Alum- Rosin, is being followed since a long time and well established in paper industries. Some adverse affects on equipments and paper quality were observed with acid sizing and to over come the adverse affects, the trial on laboratory scale were conducted continuously to search the other suitable sizing agents. Most of the mills have adopted neutral / alkaline sizing process. After making successful trial in laboratory and plant, only few agro base mills are using alkaline sizing due to inadequate system of raw material storage, preparation and improper cooking practices.

Certain problems are being faced with disperse rosin PAC sizing system, like foaming tendency at paper machine wet end at neutral pH which affect the run-ability and quality of paper. These problems may be due to poor quality of sizing chemicals and presence of certain chemicals which carry over with pulp for pulp mill and other input used for different purposes. These conditions may require use of suitable

defoamer, optimization of process parameters and selection of correct dosing input points.

The present case study on alkaline sizing envisages one such improvement that is considered non-viable till date in agro-based pulp & paper small scale mills. The alkaline sizing has its own advantages to improve the quality of paper in comparison with acid & neutral sizing. The purpose of the study to produce the high bright paper with more permanency with out increasing chlorine consumption, pollution load and without any impact on sizing cost.

SIZING

Sizing is defined as the process in which a chemical additive, usually an aqueous liquid, provides paper & paperboard with resistance to wetting and penetration. Cellulose is a hydrophilic natural compound and pulp fiber surfaces have a high specific energy. Thus, water easily penetrates through it. Various sizing agents (viz. rosin, paraffin waxes, wax derivatives,

wax emulsions, & synthetic sizing agents) have been developed to make paper reasonably hydrophobic.

Sizing can be applied internally or externally, thus called as internal or external sizing. Mainly three type of internal sizing are being used in paper manufacturing i.e. acid sizing, neutral sizing and alkaline sizing. In internal sizing the sizing chemicals are added and mixed properly in pulp whereas in external sizing the sizing chemicals are applied on the surface of paper.

ACID SIZING (ALUM-ROsin SIZING)

Acid sizing is most adopted sizing process in the mills throughout the world. Manufacturing of paper with modern technology was started first with acid sizing way back in 1807. But acid sizing came into picture in 1950s. It gained its popularity throughout the world and was the first choice of papermaker. This sizing process is cheap, reliable and reasonably effective. It involves the internal addition of partially or completely

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saponified rosin called rosin size. The rosin sizing process involves the separate addition of rosin and alum.

Now a days fortified rosin is more popular because it having three carboxylic groups in comparison to rosin soap having single carboxylic group. Rosin has been reacted with fumaric acid or maleic anhydride to form the Diels-Alder adduct. The reacted product contains extra carboxyl groups and produces more efficient sizing response than the un-reacted rosin acids. pH value in acid sizing is maintained 4.0 to 5.0. Fortified sizes are more anionic, tend to form smaller particle sizes and are thereby distributed over the fiber surfaces more widely and uniformly.

STRENGTH PROPERTIES AND CONSUMPTION PARAMETERS WITH ACID SIZING

The alum-rosin sizing was started during commissioning of the mill in May, 2005. The consumption of Fortified rosin & alum along with strength properties and process parameters are tabulated as below -

S.No	Parameter	Unit	Jun-05	Jul-05
1	Alum Consumption	%	4.6	4.5
2	Fortified Rosin	%	1.1	1.2
3	Back Water pH	-	5.5	5.4
4	FPR	%	69.5	70.8
5	Brightness	%	80.0	80.0
6	Cobb Value	g/m ²	24	24
7	Tear Index	MD	4.13	3.70
		CD	5.00	4.80
8	Tensile Index	MD	44.1	45.5
		CD	19.2	20.8
9	Wax Pick	No.	9A Clear	9A Clear

Table No.- 01

THE COST OF ALUM ROSIN SIZING WAS RS. 550 PER TONNE OF PAPER, INCLUDING RETENTION AID

Back Water			Cobb Value		Brightness (%)	PAC (kg/MT)	Dispersed ROSIN (kg/MT)
pH	Acidity (ppm)	FPR (%)	T/S	W/S			
6.07	19.6	73.2	22.0	24.0	82.0	35.1	25.5
5.80	17.0	75.4	21.0	23.0	82.4	36.2	25.4
6.51	12.1	77.5	21.0	23.0	82.7	35.5	22.9
6.45	19.0	74.9	21.0	23.0	82.9	37.1	23.4

Table No.- 02

THE COST OF DISPERSE ROSIN- PAC SIZING WAS RS.860 PER TONNE OF PAPER, INCLUDING RETENTION AID

ADVERSE AFFECTS OF ACID SIZING-

- Faster Colour Reversion
- Corrosion problem at wet end
- Chocking of machine Clothing (Wire & Felts)
- Less optical Properties
- Drop in brightness in pulp to paper (4 to 6% ISO)
- Less Permanency
- Reducing strength properties
- Poor paper machine run-ability
- Fluff problem in paper

NEUTRAL SIZING (DISPERSED ROSIN SIZES)

The developments & discoveries in sizing started with development in paper manufacturing with technological improvements. The dispersed rosin size was used in which the dispersed size particles are stabilized by surfactants, starch, polymers or proteins. Rosin soap sizes are replaced by dispersed rosin because of inflexibility of pH and hard sizing was not easily achieved.

Anionic dispersed rosin sizes contain 95-100% free rosin acid which emulsified in water at 35% solids and stabilized by anionic surfactants or proteins. The pH range of Anionic dispersed rosin sizing is 5.5-6.5. Dispersed anionic rosin required less Alum in comparison to rosin soap.

Cationic dispersed rosins are 100% free rosin acid which emulsified 35% and stabilized with cationic polymers. Handling and addition is same as anionic dispersed rosins. The pH range of cationic rosin sizing is 5.5-6.5. PAC can be used in place of alum as the drop in pulp to paper brightness is less.

POLY ALUMINUM CHLORIDE (PAC)

It is a polymerized aluminum chloride which is a good coagulant and also having the property to act as anti slime in the system. Now a days PAC is being used as a replacement of Alum because it is having Chloride ions in place of sulphate ions and there is no formation of aluminates resulting less chances of clothing choking and press picking. Dispersed rosins and fortified rosins are more effective with PAC.

FACTOR AFFECT NEUTRAL SIZING

- Stock temperature
- High sulphate ions
- High Calcium ions
- Over bleached pulps
- More refining

The Plant Trial Observations Are Tabulated in table no. 02

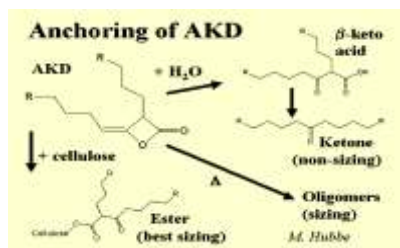
It is clear from the data that there is gain in brightness, FPR and pH of paper, but the cost of sizing was observed very high. Therefore the neutral sizing was not commercially viable.

SYNTHETIC SIZING (AKD AND ASA)

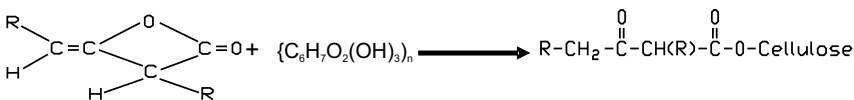
AKD appeared in the Patent literature in 1953 and in the open literature 1956. The other common synthetic sizing agent ASA (Alkenyl Succinic anhydride) was first synthesized in 1974. From 1956 to early 1980 these materials were adopted for use in certain specialty grades where very hard sizing was needed such as liquid packaging grade. Now a days situation is changed as market demands good quality of paper, high opacity and high

brightness. By 1994 the percentage of AKD and ASA had grown to over 90 % in US. In India ASA and AKD come into the picture after 1990 and grown up after 2000.

Various synthetic sizing agents have been introduced that react chemically with the hydroxyl groups of cellulose fibers and thus become permanently anchored. The chemical reactivity of these additives offers several advantages to the papermaker. In principle, a mono-molecular layer of a firmly bound sizing agent with its hydrophobic subsistent oriented away from the cellulose substrate should provide excellent water repellency. In practice, chemically reactive sizing agents are generally much more effective than rosin size per kilogram added, because of stronger (chemical) bonding and better (mono layer) distribution. Excellent sizing is obtained at addition levels as low as 0.05% concentration. However, these synthetic materials are also more expensive than rosin. Since chemically reactive sizing agents do not require alum as a coreactant, Retention aid or bonding link to cellulose can be used in neutral- to - alkaline papermaking systems, thus reducing equipment corrosion and producing paper with better long term strength. In general these chemical additives react with cellulose more rapidly under alkaline conditions. Those based on fatty acids make paper surface slippery, but various anti-slip agents can be added to the formed sheet to counter this effect. These sizing agents are generally added internally, but they can be employed in the surface sizing of paper.



Alkyl Ketene Dimer (“Aquapel”) is the most commonly used chemically reactive sizing agents. The ketene dimer molecule consists of two hydrocarbon chains each of 16 to 18 carbon atoms in length, attached to a 4-membered lactone ring under neutral or alkaline conditions the lactone ring will open and react with materials containing active hydrogen substituents. In particular the ketene dimer will react with cellulose hydroxyl groups to form a stable ester linkage as shown below.



“Aquapel” is supplied as an aqueous suspension of Alkyl Ketene Dimer particles, stabilized by a cationic starch. The cationic stabilizer also serves as retention aid that helps attach the particles to the anionic fiber surfaces. Although the ketene dimer molecule will also react with water, its long hydrocarbon chains apparently protect the very active lactone ring quite effectively. When added internally about two thirds of the retained material will react with cellulose rather than from the ineffective hydrolysis product, a ketone.

The low melting point of “Aquapel” (40 to 50°C) permits this sizing agent to spread over the fiber surfaces very extensively during the elevated temperature drying of the paper. The resulting monomolecular film becomes tightly bound to the cellulose substrate by chemical reaction during the drying process off machine sizing is good, but the ultimate sizing level is achieved gradually during room temperature aging or rapidly by elevated temperature curing. Used as a close internal sizing agent. Sizing agent may be used as closed as possible to the head box. Excellent sizing efficiency is obtained by the use of 0.05 to 0.3% “Aquapel” in a neutral to alkaline environment (pH 6.5 to 8.5). The presence of alum in this sizing system interferes with the reaction of the ketene dimer with cellulose.

THE BASIC REQUIREMENTS FOR ALKALINE SIZING

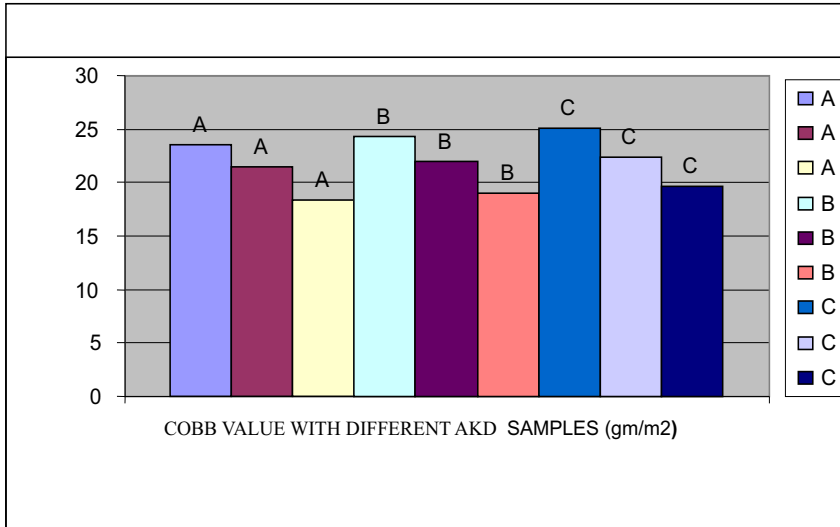
- **High retention of fibers & fillers:-** Since AKD is nonionic molecules that have no attraction for anionic fibers & other substances, such as cationic starch and synthetics Cationic Polymers must be used as size retention aids.
- **Uniformly distributed on fiber surfaces:-** AKD is water insoluble at room temperature depending upon the length and degree of un-saturation of their hydrocarbon chains. To get good distribution on fiber surfaces, the liquid or solid must be sub-divided into very small (submicron) particles. Dilute suspensions (emulsion) of these small particle are then added to the paper making

system with uniform mixing. The second feature that contributes to good distribution is that retained size particles melt and spread over fiber surfaces- similar to dispersed rosin sizes.

- **Able to produce hydrophobic fiber surfaces:-** AKD molecules contain relatively inert hydrocarbon chains that impart hydrophobic character to the materials and enable them to do same for fiber surfaces
- **Adhere strongly to fibers:-** AKD molecules contain reactive centers that react with the fiber surface hydroxyl groups to form covalent linkages that are stable in the presence of water and anchor the size molecules to fibers.
- **Chemically inert to the penetrants:-** AKD is capable of providing sizing agent more aggressive liquid than rosin sizes. This is a result of their strong bonding to fiber surfaces and the ability of their hydrocarbon chains to affect large area of the fiber surfaces.
- **Stability of emulsion being used in system:-** AKD can also react with hydroxyl group of water. A Palmitone acid is produced after reaction with water which do not contribute to the sizing and their presence reduces the efficiency of an AKD emulsion. Hence forth the self life of AKD is approximate ten days at normal temperature and held for months at freezing temperature.
- **Selection of suitable calcium carbonate filler:-** As fillers adversely effect the sizing performance of all sizes because fillers are having higher specific surface area than fibers. PCC filler is reduced the sizing demand in comparison to GCC.
- **Selection of suitable/ compatible dyes:-** Dyes have to be selected those which give good results on higher pH that is 7.5 -9.0 and having good dispersing property.

Samples	AKD (Kg/ton)	Fixing Agent (gm/ton)	Retention Aid (gm/ton)	Cobb Value (gm/m ²)
A	12	400	250	23.5
	15	400	250	21.5
	18	400	250	18.4
B	12	400	250	24.3
	15	400	250	22
	18	400	250	19
C	12	400	250	25.1
	15	400	250	22.4
	18	400	250	19.7

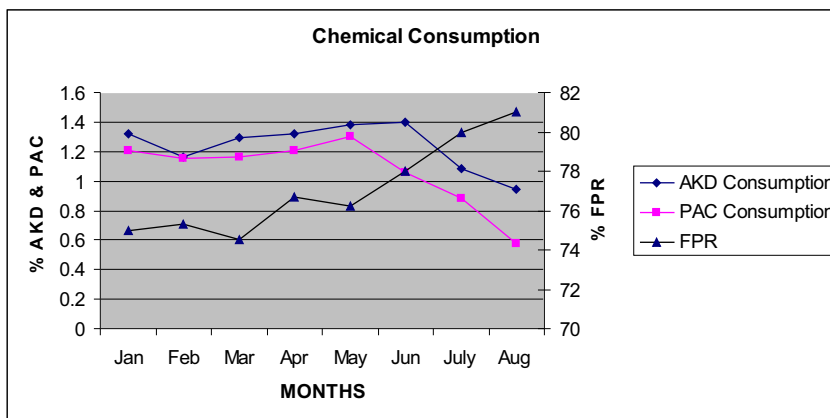
Table No.- 03



THE CHEMICALS CONSUMPTION OF AKD SIZING (MONTHLY AVERAGE 2007)

S.No.	Parameter	Unit	Jan	Feb	Mar	Apr	May	Jun	July	Aug
1.	AKD Consumption	%	1.32	1.16	1.29	1.32	1.38	1.40	1.08	0.94
2	PAC Consumption	%	1.21	1.15	1.16	1.21	1.30	1.06	0.88	0.58
3	Back Water PH	-	7.5 - 7.7	7.5 - 7.7	7.5 - 7.7	7.5 - 7.7	7.5 - 7.7	7.5 - 7.7	7.6 - 7.8	7.6 - 7.8
4	FPR	%	75.0	75.3	74.5	76.7	76.2	78.0	80.0	81.0
5.	Alkalinity	ppm	140	150	160	150	140	170	180	190

Table No.-04



- **Selection of suitable deposit control programme:-** As alkaline sizing having the whole system pH range 7.0-9.0 therefore there is more chances for slime generation and deposit in the system. We have to select suitable deposit control programme.
- **Boil out Programme:-** Whole system have to be boiled out with caustic, anti slime and surfex (detergent) to clean the system periodically.

LABORATORY TRIALS- The AKD samples were collected from three different manufacturers along with ATC and retention aid chemical. Wheat straw mix bagasse pulp was collected from pulp mill and evaluated in laboratory with different dosing of AKD. The results are tabulated in table No. 03.

Based on the above results, it was found that 'Sample A' is suitable for our requirements of AKD sizing. On the basis of these results the AKD sizing was started in plant in the month of October 2005 and are getting excellent results since then. The results of last eight months are tabulated on average basis in table No. 04.

As it is evident from the data presented in this paper, the alkaline sizing is beneficial in all aspects of paper manufacturing. The paper strength properties, brightness, whiteness, permanency, shade and pH of paper are improved in alkaline sizing.

COST COMPARISON: - The AKD sizing cost is almost equal to acid sizing where as neutral sizing cost is higher. Cost of sizing can be reduced by optimization of chemicals dosing and process parameters which varies mill to mill.

ADDITIVES BENEFICIAL FOR AKD SIZING

- Wet strength resins
- Retention aids
- Drainage and drying aids
- Dry strength resins
- Cationic starch

These additives are all cationic materials that act primarily by improving size, fines, and/or filler retention.

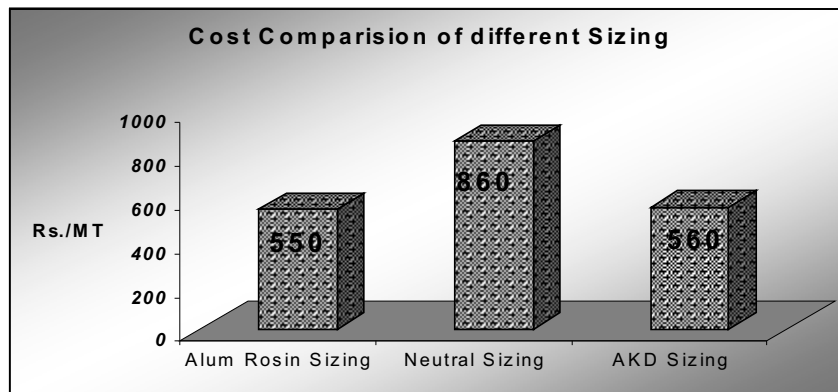
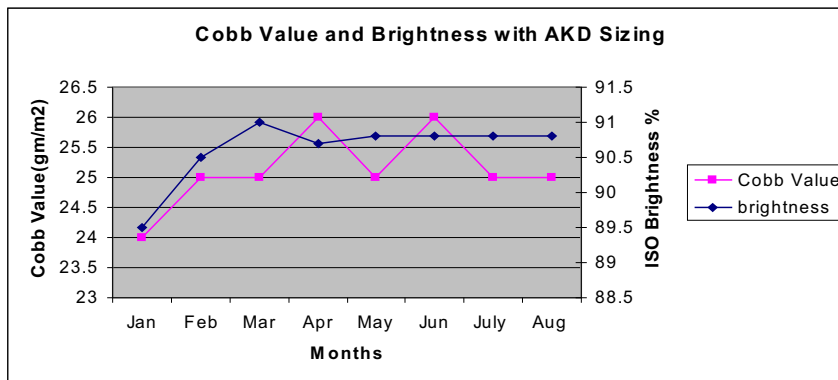
PAC does not enhance the effectiveness

PROPERTIES OF PAPER WITH AKD SIZING (MONTHLY AVERAGE -2007)

S. No	Parameter	Unit	Jan	Feb	Mar	Apr	May	Jun	July	Aug
1	Optical Properties									
	i. Brightness ISO	%	89.5	90.5	91.0	90.7	90.8	90.8	90.8	90.8
	ii. a Value		4.4	4.5	4.5	4.5	4.4	4.4	4.4	4.4
	iii. b value		-9.7	-10.1	-10.1	-10.1	-10.4	-10.4	-10.4	-10.4
2	Cobb Value	gm/m ²	24	25	25	26	25	26	25	25
3	Tear Index MD	mN.m ² /g	3.6	3.8	3.7	3.6	3.7	3.8	3.7	3.8
	CD		4.4	4.5	4.5	4.5	4.4	4.4	4.4	4.4
4	Tensile Index									
	MD	Nm/g	43.60	41.39	42.60	41.90	42.52	42.79	43.19	42.2
	CD		24.55	23.31	24.15	22.98	23.56	23.87	22.97	22.2
5	Wax Pick	No.	12A Clear	12A Clear	12A Clear	12A Clear	12A Clear	12A Clear	12A Clear	12A Clear
6.	Stiffness MD	mN	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
	CD		2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5

Table No.- 05

THE COST OF AKD SIZING IS RS. 560 PER TONNE OF PAPER, INCLUDING RETENTION AID.



Cooking Parameters

S.No	Parameter	UOM	Jan	Feb	Mar	April	May	June	July	Aug
1	Raw Material:									
	- Bagasse	%	79.2	95.2	100	100	100	78.2	70.0	52.0
	- Wheat Straw	%	20.8	4.8	-	-	-	21.8	30.0	48.0
2	Alkali as NaOH	%	13.14	13.07	13.06	13.08	13.11	13.47	13.65	13.4
3	Cooking Aid	%	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
4	Bath Ratio	-	1:4	1:4	1:4	1:4	1:4	1:4	1:4	1:4
5	Cooking Cycle	Min.	21	21	20	21	20	20	20	20
6	Cooking Temp.	°C	160-165	160-165	160-165	160-165	160-165	160-165	160-165	160-165
7	Kappa Number Of Screened Pulp	No.	14-15	14-16	14-16	13-15	13-15	13-15	14-16	14-15

Table No.- 06

of AKD sizes directly. In fact, there is evidence that PAC is detrimental in this regard. PAC is used in alkaline papermaking for the neutralization of interfering substances and can improve AKD sizing by this, indirect route. It is important that the PAC and AKD addition points are well separated and PAC overdosing should be avoided.

DOSING POINTS SELECTION

Dosing point of each chemical have to be selected according to efficiency of chemical reactivity and reaction time. The dosing point of different chemicals are given as below (in NTL).

- ACT-Bagasse Chest
- OBA- Mixing Chest
- DYE- Mixing Chest
- CATIONIC STARCH- Mixing Chest
- DRY STRENGTH RESIN- Machine Chest
- AKD- Machine Chest
- PAC-Primary centricleaner reject pit
- RETENTION AID CHEMICAL- Pressure screen in-let

ADVANTAGES OF AKD SIZING

- Increase equipment life due to less corrosion at higher pH.
- Increase in brightness and optical properties.
- Increase in Permanency of paper.
- Increase in machine clothing life due to less chocking.
- GCC/PCC can be used as filler.
- Gain in machine run-ability due to better drainage
- Good smooth feeling on paper surface.
- Reduction in Fluff.
- More FPR of fiber and ash than acid sizing.

KEY POINTS FOR AKD SIZING SUCCESS

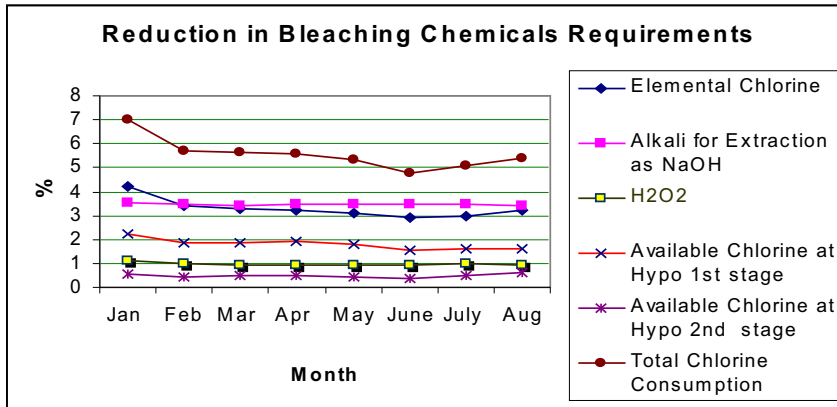
It is learnt from the study of plant trail that alkaline sizing is beneficial in today's competitive market in Agro base Plant. To make it success in any mill, there are some Key points, as given below

- Preparation of raw material is very important to produce good quality of pulp and minimization of fines content.
- Entering of water in wheat straw stack is poison and in case of

BLEACHING PARAMETERS

S. No	Parameter	UOM	Jan	Feb	Mar	Apr	May	June	July	Aug
1.	Elemental Chlorine	%	4.20	3.44	3.30	3.21	3.10	2.90	3.0	3.2
2	Alkali for Extraction as NaOH	%	3.53	3.46	3.44	3.47	3.48	3.49	3.50	3.43
3	H ₂ O ₂	%	1.13	1.00	0.90	0.92	0.96	0.95	0.98	0.96
4	pPH at Alkali Mixture	-	10.0-10.5	10.0-10.5	10.0-10.5	10.0-10.5	10.0-10.5	10.0-10.5	10.0-10.5	10.0-10.5
5	Available Chlorine at Hypo 1 st stage	%	2.24	1.83	1.86	1.90	1.77	1.52	1.60	1.60
6	Available Chlorine at Hypo 2 nd stage	%	0.56	0.46	0.47	0.48	0.44	0.38	0.50	0.60
7.	Total Chlorine Consumption	%	7.0	5.73	5.63	5.59	5.31	4.80	5.1	5.4

Table No.- 07



STRENGTH PROPERTIES OF FINAL PULP

S.No.	Parameter	Unit	Jan	Feb	Mar	Apr	May	Jun	July	Aug
1.	Brightness	%	84 - 86	84 - 86	85 - 87	85 - 87	86 - 87	86 - 87	86 - 87	86 - 87
2	Tear Factor	-	51.3	51.6	49.0	48.1	47.9	50.2	50.5	50.3
3	Breaking Length(Avg.)	Mts.	3990	3650	3620	4040	3880	3610	3600	3500
4	Freeness(Avg.)	^o SR	29	29	26	20	18	19	21	21
5	Viscosity (Avg.)	CPs	11	11	10	12	12	12	12	12
6	Copper Number (Avg.)	-	0.7	0.6	0.7	0.8	0.7	0.8	0.8	0.8
7.	Fiber Classification	+30 +50 +100 +200 -200	24.0 12.0 29.0 16.0 19.0	21.0 15.0 29.0 16.0 19.0	25.0 16.0 26.0 15.0 18.0	26.0 15.0 26.0 16.0 17.0	24.0 17.0 24.0 18.0 17.0	26.0 12.0 28.0 16.0 18.0	24.0 17.0 24.0 16.0 19.0	25.0 15.0 24.0 16.0 20.0

Table No.- 08

- bagasse it is gift (wet bulk storage).
- Effective wet washing is the key of quality in the case of bagasse and wheat straw to remove pith, molasses, sand and other unwanted material.
- Soft cooking (kappa number:- 14 15) is favorable for better strength and low fines content in pulp. Degradation is less in bleaching with lower kappa number.
- Proper washing of pulp to avoid carry over the residual chlorine, calcium and magnesium ions.
- Optimization of AKD and PAC dosing to avoid reverse sizing.
- High alkalinity and pH is associated with laser reversion.
- Optimization of boil out frequency.
- Low Temperature of stock is

favorable.

- Charge balancing of system.
- Optimization of paper drying temperature.
- AKD can be used over a pH range of 6-9, but it is most effective at a level of 8-9.

PULP QUALITY

Agriculture residue (Wheat Straw/ Bagasse etc.) have short fiber length and low percentage of lignin, therefore are very much sensitive and degraded very fast under uncontrolled condition in cooking and bleaching. Numbers of modifications and technically changes were done in NTL to standardize process parameters. The process parameters, consumption parameters and strength properties of running year, are tabulated in table no. 06, 07, 08.

CONCLUSION

AKD sizing is the way for manufacturing of high bright paper with more permanency in Agro base paper plant. This case study confirms that the cost of AKD sizing can be optimized by making some changes in system to standardize chemical consumption and process parameters. AKD sizing cost is comparable to Acid sizing and have no risk of colour reversion, fluff generation, corrosion etc. AKD sized paper having good printability on multicolor offset printing presses, because of better surface properties against acid and neutral sized paper. Preparation of raw materials before cooking is very-very important, which is the key of pulp quality to promote better AKD sizing results.

Acknowledgement

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