Economic Utilisation of Alum In Sizing

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Laboratory experiments were conducted to study the role played by the important factors like pH, residual calcium salts in pulp and free rosin in the economic utilisation of alum.

The use of acid–alum blend containing 20% sulfuric acid had been found to be more economical for achieving a particular stock pH than alum alone. Further, the addition of alum–acid blend greatly enhanced the sizing of the hand sheets. However, at low pH (high acidity) its use resulted in deteriorated sizing.

The residual calcium salts in pulp considerably reduced the sizing due to formation of insoluble soaps. These resinates consumed 50–60% of the theoretical alum. By washing the pulp with hot water at 50—60°C, the calcium content could be reduced considerably.

A steady increase in sizing value was observed for both unbleached stocks as the pH was gradually reduced upto 5.5 at which the sizing attained its peak value. Of the three free rosin sizes *used in sizing experiments, viz., low (4.26%), medinm (18.25%) and high (32.55%), medium free rosin size resulted in better sizing for both unbleached and bleached varieties.*

The spurt in prices of the essential raw materials for paper making and the Government's restrictions on selling price of the product have necessitated the industrialists to take stern economic measures in every sphere. The ability to reduce the cost of production of paper is closely connected to the effective process control at every stage of the production of material in question and the economic utilisation of the valuable chemicals like Alum, Glue, Rosin etc. It is with the second aspect of utilising some of the valuable chemicals in the sizing operations, this paper is going to deal with. Despite the fact that the alum solution used in the process is of satisfactory quality, at times its consumption goes much beyond the normal proportion, especially, while producing bleached papers.

This article describes the detailed studies designed and conducted to throw light on the role played by the important factors like pH, Calcium content of the pulp and free rosin in the economic utilisation of alum in sizing operation to reduce the cost of production of paper without sacrificing the quality.

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Theory of Rosin Sizing

Though there are several theories regarding the role of paper maker's alum, $Al_2(SO_4)_3$, 18 H_2O in sizing, it is quite well established that it plays a dominant role. According to the Ostwald and Lorenz Electro Static Theory[1] alumina is an electro cement adhering rosin to negetive charged fibres. Price et. al.[2] established that the alum reacts with sodium resinate in aqueous media, in the absence of free salts, to form equimolar mixture of basic aluminum di-resinate and free rosin acids. This basic aluminum di-resinate, ionizes to aluminum resinate. Al Re S_2+, as the pH decreases below 7.5. This ion facilitates the retention of size precipitate on the pulp by electrostatic attraction between preferentially adsorbed hydroxyl and sulfate ions on the fibres and this positive ion. The convalent nature of the aluminum resinate bonds enhances the hydrophobicity of rosin and thereby promotes sizing[3] after drying.

Experimental

Process water was used in sizing experiments and in the preparation of solutions used in the

titration. Paper Maker's alum, supplied by Dharamsi Morarji Chemicals, containing 17% Al_2O_3 and no free acid was used in these experiments. Other Inorganic Chemicals, such as Sulphuric Acid, Calcium Carbonate used in the experiments were of Analar Grade. Rosin soaps were prepared in the Laboratory from N wood rosin which had an acid no. of 165.

Sizing Studies

The pulp was beaten in a valley-beater, at 1.5% consistency to a SchopperRiegler freeness of 40°. In each batch of sizing experiments, 10.0 grams of O.D. beaten pulp was first diluted to 2 litres and properly slushed in the pulp-disintegrator. The requisite quantity of rosin (0.5% and) 1.0%) was added to the pulp and sufficiently mixed and finally the alum solution was run in to the stock to obtain the desired pH value. The volume of the alum solution consumed was recorded. Sheets of 65 and/or 135 gsm were made on a British Standard Sheet Maker which had a provisionfor back-water circulation. The back-water pH, corresponding to the pH of the stock, was maintained by the addition of sulfuric acid.

To establish the effect of adding sulfuric acid to alum solution to achieve a particular pH of stock instead of using alum solution alone, two different solutions were prepared by adding 10% and 20% of sulfuric acid on total weight of alum.

To elucidate the reduction of alum consumption by using small quantities of sulphuric acid, these solutions were added to different portions of the same pulp and the quantities required to attain a particular pH were measured. Sheets prepared with these pulps were tested for sizing (4). These experiments were conducted at various pH values between 4 and 6. The results pertaining to the relative consumption of sulphuric acid treated alum and the sizing of the sheets are presented in Table I and Figure 1.

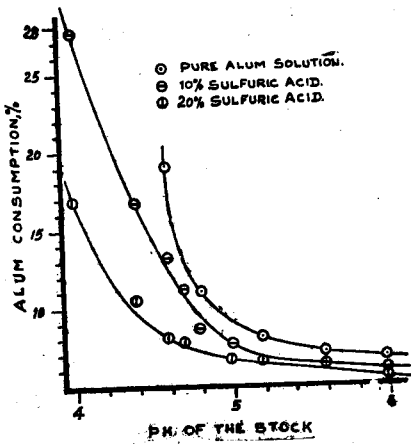

Fig. 1 Effect of Sulfuric Acid Addition on Alum Economy

Effect of the Presence of Calcium-ions on alum Consumption :

To evaluate the contribution of the Calcium content of the bleached pulp in increasing the alum consumption and in decreasing the sizing, sheets were

Table I
Effect of using Sulfuric Acid on Alum Consumption and Sizing

Sl. No.	ALUM SOLUTION AS SUCH: Alum consumption %	pH of the stock	G.S.M. of hand sheet	Sizing in seconds	10% SULFURIC ACID ADDED TO ALUM: Alum consumption %	pH of the stock	G.S.M. of hand sheet	Sizing in seconds	20% SULFURIC ACID ADDED TO ALUM: Alum consumption %	pH of the stock	G.S.M. of hand sheet	Sizing in Seconds
1.	6.8	6.0	54	8	5.83	6.0	54	17	5.64	6.0	54	20
2.	7.2	5.6	54	12	6.38	5.6	54	19	6.24	5.6	55	29
3.	8.0	5.2	54	10	7.59	5.0	54	15	6.36	5.4	54	21
4.	11.0	4.8	55	8	8.58	4.8	54.5	12	6.48	5.2	54	15
5.	19.0	4.6	55	7	11.22	4.7	54.5	9	6.60	5.0	54	14
6.	—	—	—	—	13.20	4.6	54	7	7.20	4.8	54	13
7.	—	—	—	—	16.72	4.4	54	6	7.68	4.7	54	11
8.	—	—	—	—	27.60	4.0	54	—	8.04	4.6	54	9
9.	—	—	—	—	—	—	—	—	10.44	4.4	53	8
10.	—	—	—	—	—	—	—	—	16.80	4.0	53	3

M. F. Refined-bleached Fulp Rosin addition: 0.36% Calcium content in Pulp as $CaCo_3$: 2.78%

Alum solution as such : pH : 3.6
Alum sulfuric Acid blend (20% H_2SO_4 on Alum) pH : 2.1 Tw° : 11.0
Alum-Sulfuric Acid blend (20%, H_2SO_4 on Alum)
pH : 1.8 Tw° : 12.5

prepared with various pulps containing different amounts of Calcium Carbonate at the same pH value and were tested for sizing.

The results are presented in Table II and Figure 2.

To determine the role played by the pH in alum consumption in the presence of Calcium ions, sizing experiments were also conducted with two pulp samples having different calcium content at various pH levels between 4.3 and 6. Results of these experiments are given in Tables II & IV and Figure 3.

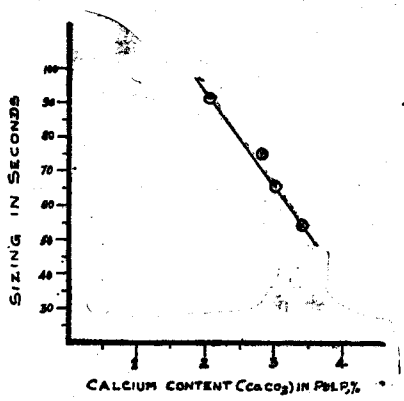

Fig. 2 Detrimental Effect of Calcium on Sizing

Sizing experiments were also conducted with the sludge-free Hypo Chlorite Solution and sludge-laden bleach liquor on two different portions of the pulp under identical conditions to find out if the turbid hypo is the

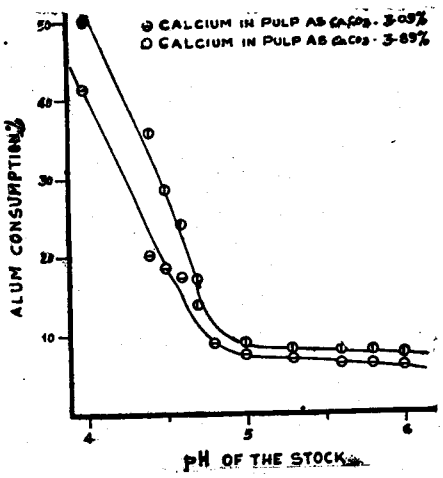

Fig. 3 Detrimental Effect of Residual Calcium in Pulp on Alum Consumption

Table II

Detrimental effect of Calcium Carbonate addition on Sizing (Figure-2)

Serial. No.	Particulars		Pulp as such 1	2	3	4
1.	pH of bleached pulp		7.7	7.7	7:7	7.7
2. a)	Calcium in pulp as $CaCo_3$.	%	2.04	2.80	3.00	3.40
b)	Calcium Carbonate added, (on O.D. Pulp basis).	%	—	0.76	0.96	1.36
3.	Rosin added	%	1.0	1.0	1.0	1.0
4.	pH of the pulp after rosin addition.	%	8,2	8.3	8.3	8.3
5.	Alum Consumption	%	7.84	11.20	14.00	17.36
6.	Final Stock pH after alum addition.	%	4.7	4.7	4.7	4.7
7.	G.S.M. of hand sheet		110	110	109	110
8.	Sizing of the hand sheet in seconds		91	75	65	54

Table III

Detrimental effect of Calcium Carbonate addition on Alum consumption and Sizing at various pH of the stock

	Bleached Pulp I					Bleached Pulp II			
Sl. No.	Alum consumption %	pH of the stock	G.S.M. of hand sheet	Sizing in seconds	Sl. No.	Alum consumption %	pH of the stock	G.S.M. of hand sheet	Sizing in seconds
1.	2.28	6.0	129	102	1.	7.92	6.0	128	49
2.	3.00	5.8	131	140	2.	8.16	5.8	131	10
3.	3.12	5.7	131	145	3.	8.40	5.7	131	107
4.	3.24	5.6	131	155	4.	8.64	5.6	129	110
5.	3.42	5.5	128	168	5.	8.88	5.5	131	1.0
6.	3.72	5.2	132	154	6.	9.36	5.2	129	9
7.	3.84	5.0	132	150	7.	12.60	5.0	129	4
8.	4.08	4.7	132	124	8.	18.0	4.7	131	8
9.	4.20	4.5	129	110	9.	24.0	4.3	130	74

Calcium content in Pulp as $CaCo_3$, 1.42%

Rosin added to Pulp : 0.5%
Alum solution: pH: 1.9; TW°:12.0
Rosin emulsion pH: 9.2
pH of process water ; 6.5

Calcium content in Pulp as $CaCo_3$:2. 5%

Rosin added to Pulp: 0.5%
Alum solution: pH: 1.9 TW°: 12.0
pH of process water : 65

Table—IV

Deterimental Effect of Residual Calcium Salts in Pulp on Alum Consumption

Sl. No.	Refined Bleached Pulp—I				Refined Bleached Pulp—II			
	Alum consumption %	pH of the stock	GSM of Hand sheet	Sizing in Seconds	Alum consumption %	pH of the stock	GSM of Hand sheet	Sizing in Seconds
1.	7.5	6.0	54	12	5.7	6.0	60	13
2.	7.8	5.8	55	13	6.0	5.8	60	15
3.	7.9	5.6	54	20	6.2	5.6	59	23
4.	8.1	5.3	56	13	6.9	5.3	59	19
5.	8.9	5.0	58.5	13	7.2	5.0	59	18
6.	9.7	4.8	55	10	8.8	4.8	59	16
7.	16.8	4.7	56	10	13.6	4.7	59	15
8.	24.0	4.6	56.5	9	17.2	4.6	60	14
9.	28.5	4.5	55	8	18.3	4.5	60	12
10.	35.7	4.4	55	7	20.1	4.4	59	10
11.	50.0	4.0	55	4	41.2	4.0	58	4
	Calcium coutent in Pulp as $CaCO_3$ % : 3.89				Calcium content in pulp as $CaCO_3$ % : 3.09			
	Alum (20% H_2SO_4) solution : pH:1.9 TW°:11.5				Alum (20% H_2SO_4) solution ; pH: 1.9 TW°:11.5			
	Rosin addition: 0.36%				Rosin addition: 0.36%			

Table V

Role of pH on Sizing (Figures 4 & 5)

Sl. No.	Alum consumption %	pH of the stock	pH of the back-water	G.S M. of hand sheet	Sizing in seconds	Alum consumption %	pH of the stock	pH of back-water	G.S.M. of hand sheet	Sizing in seconds
1.	2.73	6.0	6.1	60	12	2.82	6.0	6.0	129	102
2.	3.05	5.8	5.8	59	15	3.00	5.8	5.8	131	140
3.	3.12	5.6	5.6	60	21	3.12	5.7	5.7	132	145
4.	3.20	5.5	5.5	60	26	3.24	5.6	5.6	132	155
5.	3.25	5.4	5.4	62	24	3.42	5.5	5.5	129	158
6.	3.32	5.0	5.0	62	22	3.54	5.4	5.3	129	160
7.	3.77	4.8	4.8	65	23	3.72	5.2	5.2	132	154
8.	4.16	4.6	4.6	63	20	3.84	5.0	4.95	133	150
9.	—	—	—	—	—	4.08	4.7	4.7	134	124
10.	—	—	—	—	—	4.20	4.5	4.6	129	110
	pH of process water : 6.4					Calcium content in bleached pulp as $CaCo_3$, % 1.42				
	Rosin addition : 0.5%									
	pH of Alum solution: 0.9									

source of Calcium ions responsible for higher alum consumption and deteriorated sizing. Corresponding results are given in Table VII. With a hope that washing of bleached pulp with hot water would reduce calcium content, experiments were carried out with bleached pulp from Hypo-washer, whose calcicum content is known in the following way.

About 30 grams of O.D. pulp was taken and washed with hot water at 60°C. under suction. The washed pulp was divided into three different portions. With the first portion, the sizing studies were done after finding out the residual calcium content as calcium carbonate. The initial pH of the 2nd and 3rd pulp portions was raised to 8.8 by adding caustic solution (140 GPL) and burnt-lime (Kiln lime of purity of 70%) respectively to study the contrasting effect of high initial pH which is due to presence of calcium ions and other ions.

Further, the effect of free rosin on alum consumption was studied with bleached and unbleached kraft pulps using different rosin sizes containing 4.26%, 18.25% and 32.55% free rosin at various pH levels. For these studies requisite amount of alkali was taken in a stainless steel vessel and was melted with minimum amount of water (about 150 ml, at 90°C. To this molten alkali powdered rosin was added, while agitating mechanically. The contents were kept under agitation for 3 hours at 90°C to allow proper saponification. The total solids of the rosin soap were estimated and the free rosin content was determined using extractive method (with ether) as suggested in TAAPI Standard (5). The results are given in Table V to X.

Results and Discussion

From the results presented in Table I and Figure 1, it can be observed that the alum consumption for attaining the same pH decreases proportionately with addition of sulphuric acid to the solution.

Further, the improvement in sizing is observed with the use of sulphuric acid at the same pH of the stock as evident from the results given in Table I. The increase in sizing value due to the blending of sulphuric acid with the alum solution may be attributed to the availability of more SO_4—ions resulting from the increased dissociation of alum in addition to SO_4—ions from sulphuric acid (6). However, building up of too many SO_4—ions (high acidity at low pH) in

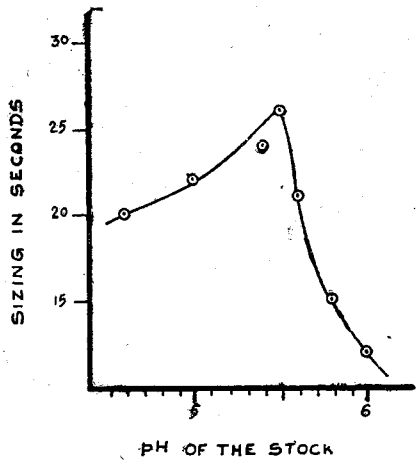

Fig. 4 Effect of pH on Sizing (Unbleached Pulp)

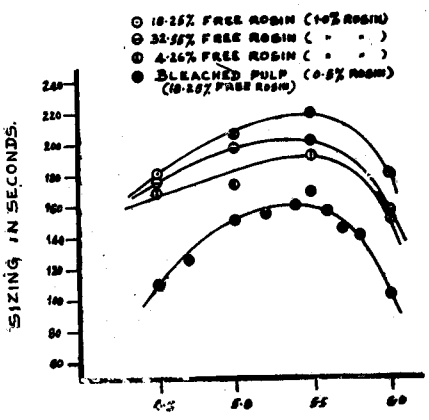

Fig. 5 Effect of pH of the Stock on Sizing

Table VI Analysis Calcium Hypo-Chlorite Sludge

Sl. No	Particulars	I	II	III	IV
1.	Clarity of Calcium Hypo chlorite solution	Very Turbid	Turbid	Slightly Turbid	Slightly Turbid
2.	Sludge present in Hypo solution (p.p.m.)	2010	1910	89.0	112.0
3.	**Analysis of Sludge :**				
a)	Loss on Ignition	33.20	29.60	—	—
b)	Calcium as $MgCo_3$, %	73 60	79.00	—	—
c)	Magnesium as $MgCo_3$, %	5.06	6.75	—	—
d)	Free calcuium oxide %	3.80	2.50	—	—
e)	Chloride as $CaCl_2$, %	1.25	1.11	—	—

Table—VII

Effect of Turbidity of Hypo-Chlorite Solution on Alum Consumption and Sizing

Sl. No.	Particulars		1*	2**	1*	2**	1*	2**
1.	Clarity of Calcium Hypo-Chlorite Solution		Clear	Turbid	Clear	Turbid	Clear	Slightly Turbid
2.	Sludge	ppm	—	1910	—	890	—	112
3.	**Bleaching of Alkali Washer Pulp**							
(a)	Hypo added as available Chlorine	%	5.0	5.0	5.0	5.0	5.0	5.0
(b)	pH maintained		8.5-9.5	8.5-9.5	8.5-9.5	8.5-9.5	8.5-9.5	8.5-9.5
(c)	Buffer added as NaOH,	%	1.2	1.2	1.15	1.15	1.2	1.2
(d)	Retention time at 40°C	(mts)	105	105	105	105	105	105
(e)	Brightness of bleached pulp	%G.E	70.0	68.5	70.2	68.0	67 0	66.0
(f)	Post color number		1.902	1.936	1.57	1.59	1.6	1.69
(g)	Calcium in pulp as $CaCO_3$,	%	2.22	2.48	1.76	2.14	2.02	2.19
4.	**Sizing Studies on bleached pulp**							
(a)	pH of the bleached pulp		7.8	7.9	8.0	8.1	7.8	7.9
(b)	Rosin added,	%	0.5	0.5	0.5	0.5	0.5	0.5
(c)	pH of the pulp after rosin addition		3.4	8.4	8.4	8.4	8.4	8.4
(d)	Alum consumption,	%	10.0	11.5	8.4	9.6	9.0	9.9
(e)	Final pH of the stock		4.7	4.7	4.7	4.7	4.7	4.7
(f)	GSM of hand sheet		55	59.5	59.5	59.5	—	—
(g)	Sizing of the hand sheets in Secs.		14	15	17.0	14	—	—

Note :—1* Bleaching of Alkali washer pulp with sludge free Hypo.
2** Bleaching of Alkali washer pulp with sludge-laden Hypo.

Table VIII

Effect of Washing of Pulp And of High Initial Stock pH on Alum Consumption

Sl. No.	Particulars	I Set				II Set				III Set			
		1*	2*	3*	4*	1*	2*	3*	4*	1*	2*	3*	4*
1.	pH of the bleached pulp	7.5	7.5	—	—	7.9	7.8	—	—	8.0	8.0	—	—
2.	Calcium content in pulp as $CaCO_3$	1.54	0.7	—	1.80	1.76	0.87	—	1.82	1.68	0.89	—	1.60
3.	Alkali as NaOH required to raise the pH to 8.8,%	—	—	0.28	—	—	—	0.148	—	—	—	0.148	—
4	Lime (70% ava. CaO) added to raise the pH to 8.8,%	—	—	—	1.12	—	—	—	1.00	—	—	—	0.90
5.	Rosin added,%	0.5	0.5	0.5	0.5	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
6.	pH of pulp after rosin addition	8.4	8.4	8.8	8.8	8.4	8.4	8.8	8.8	8.2	8.2	8.7	8.8
7.	Alum consumption, %	8.7	7.8	8.0	10.5	10.0	8.0	8·5	12.0	9.0	7.0	7.5	9.0
8.	Final pH of pulp	4.4	4.4	4.4	4.4	4.4	4.4	4.4	4.4	4.4	4.4	4.4	4.4
9.	GSM of Hand-sheet	53	59.5	59.5	60	60	60	60	60	60	60	60	60
10.	Sizing of Hand sheet in Seconds	14	32	30	23	25	33	31	25	25	34	30	24

1* Bleached pulp from Hypo washer (as such).
2* Bleached pulp washed with hot water at 60°C.
3* Pulp after washing with hot water at 60°C treated with NaOH to 8.8 pH
4* Pulp after washing with hot water at 60°C, treated with lime to pH 8.8.

Table IX

Effect of Free Rosin on Alum Consumption And Sizing (Bleached Pulp)*

Sl. No.	PH of the pulp stock	4.26% Free Rosin						18.25% Free Rosin						32.55% Free Rosin					
		0.5% Rosin				1.0% Rosin				0.5% Rosin				1.0% Rosin				0.5% Rosin			1.0% Rosin
		Alum added %	pH of back water	GSM	Sizing in Secs.	Alum added %	pH of back water	GSM	Sizing in Secs	Alum added %	pH of back water	GSM	Sizing in Secs.	Alum added %	pH of back water	GSM	Sizing in Secs.	Alum added %	pH of back water	GSM	Sizing in Secs.	Alum added %	pH of back water	GSM	Sizing in Secs.
1.	6.0	5.20				5.20				6.00				6.00				6.63							
(a)			6.1	70	2		6.0	69	11		6.0	70	5		6.0	70	32		6.0	71	4				
(b)			6.0	140	48		6.0	140	97		6.0	139	94		6.0	138	178		6.0	139	43				
2.	5.5	6.00				6.00				7.22				7.22				8.19							
(a)			5.5	70	5		5.0	71	17		5.5	70	24		5.5	69	41		5.5	19	7				
(b)			5.5	142	66		5.0	141	108		5.5	139	148		5.5	138	190		5.5	141	70				
3.	5.0	6.50				6.50				9.80				9.80				12.74							
(a)			5.0	70	3.5		5.0	71	15		5.0	69	15		5.0	70	37		4.9	71	6				
(b)			5.0	140	50		5.0	140	67		5.0	139	141		5.0	139	183		5.1	141	63				
4.	4.5	10.53				10.53				13.3				13.3				27.30							
(a)			4.5	69	3		4.5	72	11		4.6	69	22		4.5	70	33		4.5	72	4				
(b)			4.6	142	45		4.5	141	60		4.5	140	135		4.5	139	177		4.5	140	56				

Free rosin in Rosin Size : 4.26%
on 72.0% Total solids.
Rosin Emulsion : pH : 8.4
pH of Alum solution: 0.9

Free rosin in Rosin Size: 18.25%
on 81% Total solids.
pH of Rosin emulsion : 8.5
pH of Alum solution : 0.9

Free Rosin in Rosin size : 32.55%
on 72.41% Total Solids.
pH of Rosin Emulsion : 8.7
Total solids : 22.gpl

*Calcium content in bleached pulp as $CaCO_3$: 2.50%.

Table X

Effect of Free Rosin on Alum Consumption and Sizing (Unbleached Pulp)

Sl. No.	pH of the Pulp Stock	4.25% FREF ROSIN								18.25% FREE ROSIN								32.55% FREE ROSIN							
		0.5% Rosin				1.0% Rosin				0.5% Rosin				1.0% Rosin				0.5% Rosin				1.0% Rosin			
		Alum added %	pH of back water	G.S.M.	Sizing in seconds	Alum added %	pH of back water	G.S.M.	Sizing in sec.	Alum added %	pH of back water	G.S.M.	Sizing in sec.	Alum added %	pH of back water	G.S.M.	Sizing in sec.	Alum added %	pH of back water	G.S.M.	Sizing in Sec.	Alum added %	pH of back water	G.S.M.	Sizing in sec.
1.	6.0	5.85	—	—	—	5.85	—			5.5	—	—	—	5.5	—	—	—	5.20				5.20			
a)	—	—	6.1	66	4		6.0	65	26	—	6.2	67	17	—	6.0	65	35	—	6.1	65	10		6.0	65	24
b)	—	—	6.1	135	54	—	6.0	137	151	—	6.0	138	163	—	6.0	132	179	—	6.0	135	145	—	5.9	135	156
2.	5.5	6.63	—	—	—	6.60	—	—	—	6.60	—	—	—	6.60	—	—	—	6.50	—	—	—	6.50	—	—	—
a.	—	—	5.6	65	20	—	5.5	65	41	—	5.5	64	43	—	5.5	64	47	—	5.5	65	28	—	5.4	65	34
b.	—	—	5.5	135	141	—	5.6	139	191	—	5.5	136	202	—	5.5	134	220	—	5.5	139	200	—	5.5	135	202
3.	5.0	7.41	—	—	—	7.41	—	—	—	7.28	—	—	—	7.28	—	—	—	7.02	—	—	—	7.02	—	—	—
a.	—	—	5.0	65	12	—	4.9	65	30	—	5.0	65	35	—	5.0	65	38	—	5.0	65	26	—	5.1	65	29
b.	—	—	5.0	135	112	—	5.0	132	173	—	5.0	135	196	—	5.0	135	206	—	5.1	139	189	—	5.0	135	197
4.	4.5	14 69	—	—	—	14 47	—	—	—	8.85	—	—	—	8.85	—	—	—	8.45	—	—	—	8.45	—	—	—
a.	—	—	4.5	65	1	—	4.5	65	26	—	4.6	66	30	—	4.5	69	32	—	4.6	65	24	—	4.6	65	27
b.	—	—	4.5	139	105	—	4.5	139	168	—	4.6	135	192	—	4.5	135	180	—	4.5	139	170	—	4.5	139	174

Free Rosin in Rosin Size : 4.26%
on 72.0% Total solids
Rosin Emulsion: pH. 8.4
pH of Alum solution: 0.9

Free Rosin in Rosin Size: 18.25%
on 81.0% Total solids
Rosin Emulsion: pH 8.5
pH of Alum solution: 0.9

Free Rosin in Rosin Size: 32.55%
on 72.41% Total solids
Rosin Emulsion: pH: 8.7
Total solids: 22 gpl.

the closed white water system results in deteriorated sizing, This may be due to the undesirable increase of acid concentration beyond certain limits which reduces the number of positively charged Alum+++ ions which are required to form aluminum resinate (Al Re S_2+) for better sizing (7).

It may also be noticed from the results that the best sizing is attained in the region of pH of 5.6.

From the data furnished in Table V it may be noticed that the pH of the stock seems to have a dominant role in sizing of the final sheets. A steady increase in sizing value is observed for both unbleached and bleached hand sheets as the pH is gradually reduced upto 5.5, at which the sizing value attained its peak. No improvement in sizing value is obtained by further lowering the pH of the stock below 5.5 (8). Instead, a drop is observed as shown in Figures 4 & 5. Further, a close examination of the data reveals that better sizing is obtained with unbleached pulp, in which the water solubles are retained to a greater extent (3). (Water solubles in unbleached kraft pulp). This is 9% as compared to 3.89% in bleached kraft pulp). This is in agreement with the findings of E.J. Vandenberg et. al.

Deterimental Effect of Calcium ion on Alum Consumption and Sizing :

The results presented in Tables III & IV pertain to the detrimental effect of the presence of Calcium ion in bleached pulp on alum consumption and sizing. The alum requirement to obtain a particular pH increased with increase in Calcium ion concentration. Below pH 5.0 the increase in alum consumption is very sharp. This can be evidenced from the titration curves presented in Figure 3, for bleached pulps having high Calcium content.

From the results given in Table VIII, it may be observed that the pulp from alkali washer, when bleached with sludge laden hypo retains more Calcium than that of the portion, bleached with sludge free hypo. The presence of more calcium in bleached pulp not only promotes colour reversion as indicated by post colour number (9) but also increases alum consumption to obtain a particular pH and affects sizing adversely.

The experimental results in Table VIII show that by washing the pulp with hot water at 50,60°C, the calcium content (as $CaCO_3$) can be reduced by 50 to 60% and the corresponding alum consumption will be reduced. Further, raising the pH to 8.8 by caustic additon had not increased the alum consumption considerably, while excess of CaO added to raise the pH to 8.8 had not only increased the alum consumption but also caused poor sizing.

From these results, it may be inferred that the calcium which might be remaining with the pulp bleached with Calcium Hypochlorite, considerably reduces the sizing by its reaction with free-rosin to form, insoluble Calcium or magnesium resinates[10]. These resinates, because of their high negative mobilities, react rapidly with alum to form a positively charged aluminum resinate. In this process, both Calcium and Magnesium colloids consume 50—70% of theoretical alum and hence result in higher consumption[3]. According to E.J. Vandenberg,[3] the initial pH of the Calcium and Magnesium sols is higher than that of ordinary sodium resinate which may be responsible for higher alum consumption.

The Effect of Free-Rosin on Sizing :

The data presented in Tables IX & X refer to the effect of low and high free-rosin on the alum consumption and sizing of unbleached and bleached varieties. It is found that the use of low free-rosin size (4.26%) had resulted in considerable saving of alum in the case of bleached pulp, while high free-rosin size (32.55%) had resulted in better sizing and less consumption of alum for unbleached pulp[11]. From the Tables IX & X, it is evident that a medium free-rosin size (18—2.3%) results in better sizing for both unbleached and bleached varieties of pulp. However, the free-rosin should

not be higher than 40% (extractive method) as it results in coagulation during dilution which may start causing rosin spots in the finished paper[13].

Further, it has been noticed that the alum consumption to attain a particular pH remains independent of the quality of rosin added in the range of 0.5 to 1.0% on O.D. Pulp.

Conclusions :

1. With the addition of acid-alum blend containing 20% H_2SO_4 in place of alum solution, the lowering of pH is more effective than what can be obtained with alum laone. The addition of acid-alum blend enhances the sizing of the hand sheets. However, in a closed white water system, the high acidity of white water, due to the build up of too many sulfate ions, adversely affects sizing of paper as well as the wire-life.

2. When the calcium content of pulp is more than 1.5% the alum consumption increases beyond normal proportions and sizing is adversely affected. The alum consumption increases abnormally below a pH of 4.8. Hence maintenance of the pH of the bleached (high calcium content) pulp below 4.8 is not economical.

3. By washing bleached pulp with hot water at 50—60°C, the calcium content can be reduced to 50 to 60%, which results in considerable saving of alum solution. However, too much washing of the pulp should be avoided, as it removes water solubles from the pulp, causing reverse effect on sizing.

4. High initial pH of properly washed pulp does not seem to have pronounced effect on alum consumption, unless it is caused due to the presence of calcium ions, which has an adverse effect on sizing.

5. The control of the pH of the paper making stock between 5.0–5.5 is proved beyond doubt to be the most deffective range for best sizing.

6. While printing papers (using bleached pulp) may be advantageously sized with low free-rosin size (to the extent of 4–8%). The wrapping papers (using unbleached pulp) which require a high resistance to water absorption may be economically sized with high free-rosin (18—23%) size.

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