can aluminium chloride substitute alum in sizing operations?

JIVENDRA *
P. V. THOMAS**

Non-availdbility of alum due to restriction in the import of sulphur has created a problem for the paper industry. Here is an alterative suggested for the substitution of Alum by Aluminium Chloride.

The term sizing covers a number of paper making operations which serve to make paper resistant to penetration by water or other liquids and their vapours. Of the various methods adopted for sizing operation, engine sizing is the most common and is adopted for the purpose of this experimental work.

The main object of present engine sizing methods is to bring about an intimate coating of the individual fibres with the material which is insoluble in and repellant to water. The substance originally, and still most widely, used is Rosin. To obtain the desired results rosin size is to be precipitated by acids, acid salts or the salts of alkaline metals. The most common of precipitating agent is Alum and is widely used because of its maximum efficiency, economy and easy availability.

Because of heavy restrictions on import of sulphur, alum is no longer as freely available as it used to be, and even when available, is priced so very high that it seriously affects the economics of the Paper Industry. The state is fast reaching, if it has not already reached, when the paper industry for its survival has to find a more economic, equally efficient substitute for Alum.

Chief amongst the substitutes recommended by knowledgeable persons are Sodium Aluminate, ferric sulphate, aluminium nitrate, and Aluminium Chloride etc. Sodium Aluminate, though a good substitute, cannot replace alum completely and is useful only in admixture with Alum to a little extent. Porter and Lane have concluded that $AlCl_3$ is a good substitute for Alum but seemingly this has not been tried out on a commercial scale, perhaps because alum was freely available and there was little or no need to go in for untried substitues. Faced with an acute shortage of Alum and its irregular deliveries, considering the merits of other substitutes we undertook a series of experiments to determine feasibility of substitution of alum by aluminium chloride.

Sizing with rosin and alum has been one of the most important but complex processes of paper making over a period of 150 years. The mechanism by which alum sets rosin size, though highly important to the paper chemist, has been a very controversial subject. In spite of tremendous research work done and various theories propounded to explain its mechanism, we wonder if our present knowledge of sizing can be integrated into the form of a coherent theory. But it is certain that the mere precipitation of rosin on the fibres by electrolytes is not sufficient and trivalent elements must be present in sufficient quantities to develop the full efficiency of the size. The trivalent aluminium ion present in alum, which is interrelated with the soluble Alumina content of alum, is the active and important specie for the best sizing effect. Recent study by Exwall, Guide and Strazdins show that sizing would be developed only with more complex hydroxylated 'Al' ions and by Brosset that OH/Al ratio in the complex should approximate 2.5.

To deal with various theories propounded to explain the mechanism of sizing is beyond the scope of this paper. However, the widely accepted theories relating to the mechanism of sizing are discussed briefly to correlate the suitability of $AlCl_3$ as a substitute for alum.

The Role of aluminium ion in the formation of sizing complex

Sieber, Lorenz, and Ostwald believed that positively charged Alumina is formed by the hydrolysis of Aluminium salt $Al_2(SO_4)_3 + XH_2O - Al_2O(H_2O)X$ and this Alumina is attracted and held to the negatively charged fibres. This fibres thus take up a +ve charge which is responsible for attracting and holding the negatively charged rosin particles. To bring about the union of two normally repelling materials, the 'Al' ion has to contribute its +ve charge. Once the rosin has been retained, a certain number of 'Al' ions are needed to provide adequate linkage for the formation of a well oriented size film. Thode also believes in a positively

*Chief chemists, Seshasayee Paper Boards Ltd.
**Chemist, Seshasayee Paper Boards Ltd.

charged Aluminium Rosin complex and its subsequent absorption on cellulose as the principal mechanism for the rosin retention. The best sizing is obtained at the isoelectrical point. Too little alumina leaves the fibres and rosin negatively charged and too much Alumina makes them positively charged resulting in poor sizing in either case. The sizing is unsatisfactory at pH values below 4.0 to 4.3, as no Alumina is formed. At high pH values under alkaline conditions, the Alumina does not function as a fixing agent because of stabilising action of 'OH' ions on rosin particles. Though one of the obvious roles of Alum in sizing is to precipitate the rosin size, the chemical composition of the material for the sizing effect has not been established with certainty, but there is evidence that both free rosin and Aluminium resinate along with Aluminium Hydroxides are responsible for the satisfactory sizing. As per price, though the chemical composition of the precipitate may vary over a wide range with varying degrees of acidity and basicity, the sizing efficiency is not affected.

In addition to its role in precipitating rosin size, alum is also involved in a complex mechanism by which rosin size precipitate is attached to the fibres. In spite of many theories proposed to explain this mechanism, the retention of rosin has been diversely attributed to a physico chemical combination between fibres rosin and alum, to absorption of the Alumina by the fibre in the subsequent reaction between alum and rosin to an electrostatic attraction of the negatively charged fibres, the positively charged Aluminium Hydroxide and the negatively charge rosin, to methanical filtration process by which the Rosin would be retained like fillers. The electrostatic theory is a widely accepted one.

Wilson explains that the 'Al' ions are shared by both the rosin precipitates and the fibre thereby acting as a mutual bonding agent between the two. According to him, Rosin is easily saturated with Al ions but pulp fibres are not readily saturated unless the AL ion concentration is quite high which explains the greater than stoichiometric quantity of alum which is required for sizing. Thode believes that the hydrated 'Al' ions play an important role in changing the electrokinetic potential of the rosin size precipitate, which has a direct bearing on the optimum conditions for sizing. The alum and rosin forms a positively charged precipitate in fairly low concentration of Al ion, which is attracted by and precipitated on the—velycharged fibres. Guide also confirms that the retention of size precipipitate is a strong function of the electrokinetic potential of the precipitated particles. Cobb and Lowe believed that alum binds rosin size, through co-ordinate valency of 'Al' ions. The rosin is bound directly to the central 'Al' iron and cellulose to its Hydroxyl groups.

If we consider anyone of the above concepts of sizing, we find that the 'Al' ion derived from $AlCl_3$ which is a trivalent one possesses all the characteristics of Aluminium ion in alum and can replace the 'Al' ion derived from alum. The only hitch is with regard to the part played by 'SO_4' ions, which, despite intensive research, has remained highly controversial. In general, anions tend to lower the +ve charge on Alumina, making it much less efficient as it goes in between the −vely charged rosin and cellulose particles.

Building up of 'SO_4' ions in white water system accounts for the lowering of size value, as some of the 'SO_4' ions reduce the charge by forming a complex with 'Al' ion. This concept also indicates, however, that some 'SO_4' ions are necessary for good sizing in order to coagulate the positively charged rosin alumina complexes on fibres. Though the bivalent 'SO_4' ions significantly reduce surface potential of rosin size precipitate as measured by electrophoretic mobility, the reduction in the electrokinetic charge of the 'Al' ion does not necessarily mean a loss in its available +ve charge and sizing. Edward Strazdins has shown that for maximum sizing effects, the surface charge of 'Al' ion precipitate must be controlled and the $AlCl_3$, though it yields very highly charged precipitate, affords satisfactory sizing within a narrow pH range probably due to a high build up of +ve charge on fibres obstructing rosin retention. He feels that moderate of surface charge of 'Al' ion can be accomplished by adding strong electrolytic like Na_2SO_4 which would broaden the pH range of good sizing. Thus, we are led to believe in the concept that the 'SO_4' ion can both be useful and detrimental to sizing, depending upon the working conditions like pH, concentration of chemicals, rate of mixing, colloidal state of rosin and contact time etc.

PROCEDURE

The stock treatment of pulp was carried out in Noble Valley Beater at a consistency of 3.5% final freeness being 40° SR. The rosin was added as water soluble rosin soap at a concentration of 5% to simulate plant conditions and mixed with the stock in the beater with rosin for 10 minutes. The experiments were conducted with and without loading material. To this stuff varying percentages of Alum and Aluminium chloride were added separately with proper agitation. The stuff was diluted with fresh water. The standard hand sheets of 60 GSM were made at a consistency of 0.2%, pressed and dried on BPBMA sheet making outfit. The sheets were tested for sizing.

To study the effect of sulphate ions on the sizing efficiency varying proportions of Sodium sulphate were added before the addit.on of alum, sheets made as above and sizing value determined.

The following sets of experiments were conducted with varying percentages of Alum and Aluminium chloride.
No. 1—Varying proportion of Alum and Aluminium chloride were added separately to the stock containing 1.5% rosin with and without loading material. (Table 1).

No. 2—Above set was repeated except that the rosin content was kept at 1.2% only. (Table 2).

No. 3—Varying percentages of Alum, Aluminium chloride and a mixture of the two in ratio of 1 : 1 were added separately keeping a rosin % of 1.2 with loading. (Table 3)

No. 4—Varying percentages of alum and aluminium chloride were added to a stock with rosin content of 1.5%. Further, along with aluminium chloride, 100%, 50%, 25% and 150% of the SO_4 ions equivalent to that present in alum were added in the form of Na_2SO_4. (Table 4)

The above set of experiments were repeated several times and datas collected. As the results were practically uniform, only few results have been tabulated in this paper.

Observations :

In general, it is observed that addition of alum and of Aluminium Chloride brings about a considerable drop in the pH values and increase in sizing, but that a limit is soon reached beyond which additions have no effect and remain practically constant. In all the sets of experiments. Aluminium Chloride was found more effective both in reducing the pH and in increasing the sizing efficiency. The effectiveness was more than could be ascribed to the Alumina content in Aluminium chloride which was 22% as against 18% in the Alum used.

In most of the cases, the optimum results were obtained with 4 to 5% of Alum and 3 to 4% of Aluminium chloride. The reduction in sizing consequent to loading was observed only at the low percentage of alum and and aluminium chloride addition. The replacement of 50% of aluminium chloride by alum did not appreciably alter the results.

The experiments were done with fresh water for diluting the stocks as in Laboratory white water could not be collected and kept under circulation as at the Paper Machine. However, a few sets of experiments were repeated by using 50% water obtained by filtering the stock for dilution. Practically, very little advantage was observed and hence it was felt unnecessary to add the datas in this paper.

Regarding the effect of Sulphate ions on the sizing operation, it is observed that with 50% and 25% of the equivalent SO_4 ions present in corresponding percentage of alum when added along with $AlCl_3$ in the form of Na_2SO_4 improved sizing results were obtained. The SO_4 ion in excess to this quantity does not improve the sizing operation at all.

Conclusion :

The authors are confident that the problem arising from non-availability of alum due to the restriction in the import of sulphur could easily be solved by substituting it with aluminium chloride, which gives equally efficient results in pH as well as sizing. On the plant scale, the results are expected to be much better as white water would be under circulation. The authors propose to carry out the trials on the plant scale shortly.

Regarding the effect of SO_4 ions, if added along with $AlCl_3$, datas were found insufficient to arrive at a definite conclusion. As already discussed in the earlier paragraphs, the part played by SO_4 ion is still indefinite. Our experiments with Sodium sulphate addition indicate that addition to aluminium chloride of sulphate ion equal to about 25% of what is present in alum produces improved results. But excessive sulphate ions do not improve sizing efficiency nor do the replacement of 50% of Aluminium chloride by alum. This result confirms the view of the earlier work done that excess sulphate ions retard sizing efficiency and can perhaps be better studied while running plant trials. Detailed experimental work to determine effect of sulphate ions obtained by addition either of sulphuric acid or of sodium sulphate is in progress. But the work done so far confirms that even without the sulphate, aluminium chloride gives a good and much better result and can be used to substitute Alum.

The aluminium chloride used in the experiment was made from bauxite, which was produced by one of the leading chemical manufacturers on a small scale. The aluminium chloride available in the market used for other purposes is, however, very costly, as it is made from pure aluminium, but if bauxite is used to produce this commercial variety of aluminium chloride, its cost could be brought down to a level comparable with Alum. This is confirmed by the discussions the authors have had with the manufacturers who helped

TABLE NO. I.

1.5% Rosin with 20% loading.

% of alum and aluminium chloride.	WITH ALUM.			WITH ALUMINIUM CHLORIDE.		
	Stock PH.	Sizing in seconds.	Cobb.	Stock pH.	Sizing in seconds.	Cobb.
2 5	7.4	Nil.	85	5.8	7.5	34.8
3.0	6.3	6.0	37	4.8	11.0	29.0
3.5	5.3	9.0	32	4.5	12.0	27.5
4.0	4.5	12.0	28.4	4.2	14.0	25.0
5.0	4.3	14.5	24.0	4.0	16.5	22.0
6.0	4.2	16.0	22.0	4.0	16.5	22.0
7.0	4.0	—	—	3.9	—	—
8.0	3.9	—	—	3.9	—	—
9.0	3.9	—	—	3.9	—	—
10.0	3.9	—	—	3.9	—	—
15.0	3 8	—	—	3.8	—	—
20.0	3.7	—	—	3.7	—	—
1.5% Rosin without loading.						
2.5	7.6	3.0	50	5.8	8 5	35
3.0	6.4	8.0	35	5.1	10.0	33.0
3.5	5.8	10.0	32.5	4.4	13.0	28.0
4.0	4.7	13.0	28.5	4.2	16.0	25.0
5.0	4.4	15.0	26.0	4.0	18.0	22.0
6.0	4.2	16.0	25.0	3.9	18.0	22.0

TABLE NO. II.

1.2 2% Rosin with 20% loading.

2.0	6.6	1.0	78.0	5.6	5.0	40.0
2.5	6.3	1.0	72.0	5.4	8.0	32.0
3.0	5.6	3.0	45.0	4.5	12.0	25.0
3.5	5.3	4.0	42.0	4.3	13.0	25.6
4.0	4.8	10.0	30.0	4.2	14.0	25.0
4.5	4.4	12.0	25.0	4.0	14.0	24.0
5.0	4.3	12.0	25.0	4.0	14.0	22.7
6.0	4.1	12.5	24.0	3.9	14.5	22.0
1.2% Rosin without loading.						
2.0	6.8	Nil	86.0	5.5	5.0	37.0
2.5	5.8	4.0	39 0	4.5	10.5	30.0
3.0	4.9	7.0	35.0	4.2	11.5	29.0
3.5	4.5	10.5	30 0	4.0	12.0	29.0
4.0	4.2	10.5	30.5	4.0	12.5	29.0
4.5	4.1	12.0	29.0	3.9	12.8	28.0
5.0	4.1	12.5	28.0	3.9	13.0	26.0
6.0	3.9	12.5	27.5	3.8	13.0	26.0

TABLE NO. III.

1.2% Rosin with loading.

% of alum, aluminium chloride or the mixture added.	WITH ALUM.			WITH ALUMINIUM CHLORIDE.			WITH MIXTURE IN THE RATIO OF 1 : 1.		
	Stock PH.	Sizing in reconds.	Cobb.	Stock pH.	Sizing in seconds.	Cobb.	Stock pH.	Sizing in seconds.	Cobb.
2.0	6.7	Nil.	—	6.5	4.5	48.0	6.3	4.0	48,0
2.5	6.2	2.5	65.0	5.0	8.0	34.0	5.3	8.0	36.0
3.0	5.2	6.5	40.0	4.7	13.5	27.0	5.2	13.0	28.0
4.0	4.5	9.0	33.0	4.2	14.0	23 0	4.5	13.0	26.0
5.0	4.2	12.0	27.0	4.2	14 0	22.5	4.3	13.0	26.0
6.0	4.1	12.0	26.5	4.2	14.0	22.0	4.2	13.5	23.0

them conduct these experiments by making the aluminium chloride required. We are confident that once the paper industry takes to the use of aluminium chloride, the manufacturers would find the incentive to produce this product at a competitive price.

The Authors propose to continue this work as this may throw some more light on our problem. Meanwhile, the authors make an earnest and sincere appeal to all the illustrious paper technicians (assembled here*) to try this in their respective plants. In case, the proposition is found to be commercially feasible, all of us jointly can appeal to the Chemical Industries to take up the manufacture so that the valuable sulphur could be spared for other more important industries where indigenous replacement is not possible.

TABLE IV.

1.5 Rosin without loading—Aluminium Chloride added along with Sodium Sulphate.

% of alum or aluminium chloride added.	With Alum.			With $AlCl_3$			With $AlCl_3$ + equivalent SO_4 Ions			With $AlCl_3 + \frac{1}{2}$ the equivalent SO_4 Ions			With $AlCl_3 + \frac{1}{4}$ equivalent SO_4 Ions			With $AlCl_3 + 1\frac{1}{2}$ equivalent SO_4 Ions.		
	Stock pH.	Sizing in Sec.	Cobb.	Stock pH.	Sizing in Sec.	Cobb	Stock pH.	Size in Sec.	Cobb.	Stock pH.	Size in Sec.	Cobb.	Stock pH.	Size in Sec.	Cobb.	Stock pH.	Size in Sec.	Cobb.
3.0	7.3	8	34.0	6.0	13.5	26	6.1	15	23	5.3	20	20	5.4	20	20.2	5.3	15	23.0
3.5	6.0	12.5	28.0	4 8	17.0	21	4.8	18	21	4.8	20.5	20	4.8	21	19.3	4.8	17	21.5
4.0	5.5	14.0	25.0	4.4	19.0	19.5	4.4	21	19	4.8	22	19	4.3	22.5	19.0	4.3	19	20.0

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*Bhubaneshwar Seminar of IPPTA.