Role of Sulphamic Acid in Chlorination And Hypochlorite Stages of Hardwood Pulp Bleaching

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ABSTRACT: Based on extensive experimental work, small amount of sulphamic acid is added in hypochlorite stages of CEHH bleaching sequence in our mills for last many years. Its advantage is improved pulp viscosity even at higher brightness level of 80-82% Elrepho. This paper deals with the benefits gained by the addition of sulphamic acid in chlorination stage of bleaching sequence of mixed hardwood pulp. Laboratory experiments were conducted over wide range of sulphamic acid addition (0-6% on available chlorine) during chlorination and hypochlorite bleaching stages. The optimum dose of around 2% sulphamic acid on available chlorine in chlorination and hypochlorite bleaching stages give 25-40% improvement in pulp viscosity with better strength properties.

INTRODUCTION

Chlorine reacts with carbohydrate groups in several ways. Primary and secondary hydroxyl groups are oxidized to aldehydic and ketonic groups respectively. These oxidised groups render the carbohydrate molecule more sensitive to degradation in acid (aldehydic groups at C_6) and alkaline (ketonic groups in C_2 and C_3) medium. In addition, there is a chlorine induced cleavage of glycosidic bonds. The reduction in the viscosity of pulp is probably due to the increase in oxidised groups in carbohydrates. Agents such as sulphamic acid, chlorine dioxide etc. when added in chlorination stage oxidize aldehydic groups rendering carbohydrate chain more resistent to acid and alkaline degradation (1).

It is generally accepted that oxidation by hypochlorous acid is the mechanism behind pulp degradation (2) Tobar (3, 4) has theorised that sulphamic acid will react preferentially with small amounts of undissociated hypochlorous acid forming N-chloro and N-dichlorosulphamic acid.

$$NH_2SO_3H + HOCl = NHClSO_3 + H_2O$$
$$NHClSO_3H + HOCl = NCl_2SO_3H + H_2O$$

This effect of sulphamic acid has been carried out to its property of temporarily binding chlorine, thereby the concentration of active chemicals is evened out during the course of reaction. The chlorine in the form of these compounds is still active and forms milder bleaching agents which are less aggressive to pulp and hence decrease or eliminate degradation. This has led to the thought of using sulphamic acid in chlorination stage in the same manner that it proved efficient in hypochlorite stage.

Instead of sulphamic acid, other nitrogenous compounds such as urea, ammonium chloride etc. have been used but these compounds do not function as effective as sulphamic acid in reducing degradation (3).

Extensive amount of work has been carried out in our laboratory (5, 6) but was restricted to the addition of sulphamic acid in hypochlorite stage only. After

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establishing its suitability, it has become the common practice now to use 2-3% sulphamic acid on available chlorine during hypochlorite stages in our mill.

Earlier bamboo was the main raw material used in our mill. Presently, mixed hardwoods such as eucalyptus hybrid, casuarina (Casuarina equisitifolia), subabul (Leucaena leucaenaphala) etc. are being utilised for pulp production. All these raw materials being the source of short fibres, the ultimate aim is to avoid possible degradation of pulp during bleaching to maximum extent.

The present study deals with the use of sulphamic acid in chlorination stage also with hypochlorite stages of CEHH bleaching sequence, as has been outlined in some source of literature.

EXPERIMENTAL

Sufficient quantity of mixed hardwood pulp from Pulp Mill decker was collected to carry out bleaching experiments. The bleaching sequence chosen was CEHH in which the prime variation was the addition of different quantities of sulphamic acid in chlorination and hypochlorite stages separately as well as in all stages. To verify the contribution of sulphamic acid, the experiments were set in such a way as to use it in these stages and then comparing with the blank experiment under identical conditions of bleaching such as chemical addition, temperature, consistency, time etc.

Required quantity of sulphamic acid was added wherever required in the form of solution (10 gpl) to chlorine emulsion, hypochlorite solution just before the addition to the pulp to be bleached.

In the first set of small scale bleaching experiments, the quantity of sulphamic acid on available chlorine was varied from 0-6% in every stage. The data and results are recorded in Table No. I and fig. 1.

As observed from first set, about 2-3% sulphamic acid addition was found to be optimum and hence the second set of experiments was limited to its addition

Table 1.

Optimising Experiments on Bleaching of Pulp
Unbld. pulp Kappa No. 20.2

Sequence Code / Particulars	CEHH	C_2EHH	CEH_2H_2	C_2EH_2H	$C_2EH_2H_2$	C_4EHH	CEH_4H_4	C_4EH_4H	C_4EH_4H	C_6EHH	CEH_6H_6	C_6EH_6H	$C_6EH_6H_6$
Chlorination Stage:													
Cl_2 added, % on pulp	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Sulphamic acid, % on Cl_2	--	2.0	--	2.0	2.0	4.0	--	4.0	4.0	6.0	--	6.0	6.0
Alkali Extraction Stage:													
NaOH added, % on pulp	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Hypo I Stage:													
Hypo as av.Cl_2, % on pulp	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
Sulphamic acid,% on Cl_2	--	--	2	2	2	--	4	4	4	--	6	6	6
Hypo II Stage:													
Hypo as av. Cl_2, % on pulp	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Sulphamic acid, % on Cl_2	--	--	2	--	2	--	4	--	4	--	6	--	6
Bld. Pulp Brightness, % (Elrepho)	77.3	78.5	78.6	78.6	78.6	79.4	79.8	79.9	79.9	79.3	79.7	79.9	79.9
Bld. pulp viscosity, cP. (CED)	8.2	8.7	8.8	9.8	10.4	8.7	9.8	10.4	10.6	8.9	10.3	10.8	11.2

CONSTANT CONDITIONS	Cy., %	Temp., °C.	Retention time, Min.	pH range
Chlorination	3	Ambient	30	2.0-2.2
Alkali Extraction	5	60	60	10.6-10.8
Hypo I	10	42	90	7.0-7.5
Hypo II	10	33	60	7.5-8.0

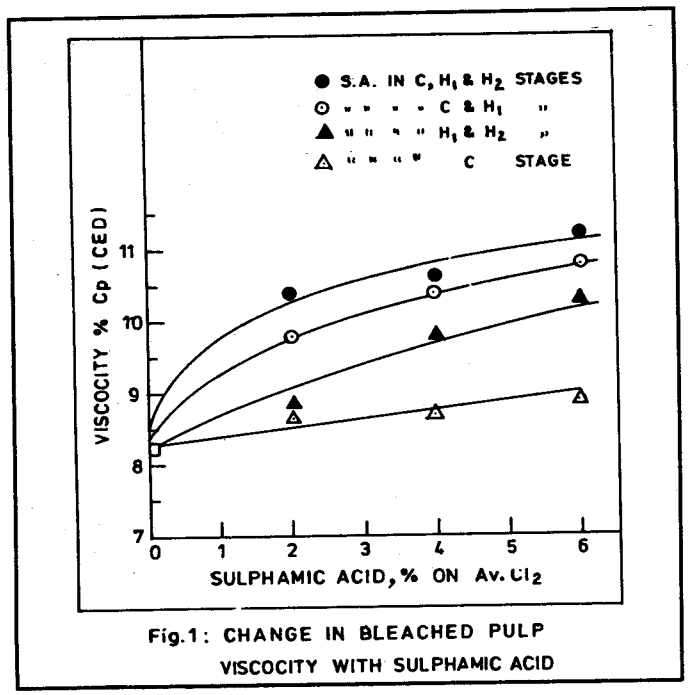

Fig.1: CHANGE IN BLEACHED PULP VISCOCITY WITH SULPHAMIC ACID

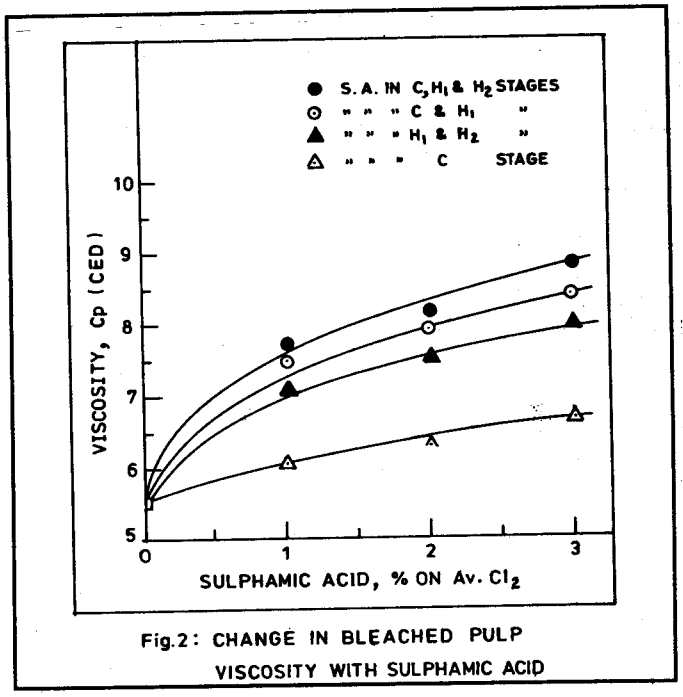

Fig.2: CHANGE IN BLEACHED PULP VISCOSITY WITH SULPHAMIC ACID

upto 3%. The data and results are as shown in Table No. II and fig. 2.

The third set of experiments included large scale bleaching using 2 and 3% of sulphamic acid on avail-

Table 2.

Small Scale Bleaching Experiments with Minimum Amount of Sulphamic Acid
Unbld. pulp Kappa No. 20.2

Sequence Code / Particulars	CEHH	C_1EHH	CEH$_1$H$_1$	C_1EH$_1$H	C_1EH$_1$H$_1$	C_2EHH	CEH$_2$H$_2$	C_2EH$_2$H	C_2EH$_2$H$_2$	C_3EHH	CEH$_3$H$_3$	C_3EH$_3$H	C_3EH$_3$H$_3$
Chlorination Stage:													
Cl_2 added, % on pulp	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Sulphamic acid, % on Cl_2	--	1.0	--	1.0	1.0	2.0	--	2.0	2.0	3.0	--	3.0	3.0
Alkali Extraction Stage:													
NaOH added, % on pulp	1.7.	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Hypo I Stage:													
Hypo as av.Cl_2, % on pulp	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Sulphamic acid,% on Cl_2	--	--	1.0	1.0	1.0	--	2.0	2.0	2.0	--	3.0	3.0	3.0
Hypo II Stage:													
Hypo as av. Cl_2, % on pulp	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sulphamic acid, % on Cl_2	--	--	1.0	--	1.0	--	2.0	--	2.0	--	3.0	--	3.0
Bld. Pulp Brightness, % (Elrepho)	78.7	79.6	80.0	79.9	80.3	80.1	80.3	80.3	80.3	80.2	80.4	80.4	80.7
Bld. pulp viscosity, cP. (CED)	5.5	6.1	7.1	7.5	7.7	6.3	7.5	7.9	8.2	6.7	8.0	8.4	8.8

CONSTANT CONDITIONS	Cy., %	Temp., °C.	Retention time, Min.	pH range
Chlorination	3	Ambient	30	2.0-2.2
Alkali Extraction	5	60	60	10.6-10.8
Hypo I	10	42	90	7.0-7.5
Hypo II	10	33	60	7.5-8.0

able chlorine in (a) only chlorination stage; (b) both hypochlorite stages, and (c) chlorination and hypochlorite stages. Large scale bleaching without addition of sulphamic acid i.e. control bleaching experiment was also carried out. All the bleached pulps were separately beaten in Laboratory valley beater to 30°SR level. Handsheets of 60 gsm were prepared on the British Sheetmaking Machine. These handsheets were conditioned to 27°C and 65% RH and the strength properties were determined. The experimental results are given in Tables III & IV and Figs. 3 & 4.

Table 3.

Large Scale Bleaching Experiments
Unbld. pulp Kappa No. 22.2

Sequence Code / Particulars	A	B		C		D	
	CEHH	C_2EHH	C_3EHH	CEH_2H_2	CEH_3H_3	$C_2EH_2H_2$	$C_3EH_3H_3$
Chlorination Stage:							
Cl_2 added, % on pulp	3.75	3.75	3.75	3.75	3.75	3.75	3.75
Sulphamic acid, % on Cl_2	--	2.0	3.0	--	--	2.0	3.0
Alkali Extraction Stage:							
NaOH added, % on pulp	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Hypo I Stage:							
Hypo as av.Cl_2, % on pulp	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Sulphamic acid,% on Cl_2	--	--	--	2.0	3.0	2.0	3.0
Hypo II Stage:							
Hypo as av. Cl_2, % on pulp	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sulphamic acid, % on Cl_2	--	--	--	2.0	3.0	2.0	3.0
Bld. Pulp Brightness, % (Elrepho)	79.8	79.8	79.7	80.3	80.3	80.5	80.5
Bld. pulp viscosity, cP. (CED)	6.4	7.7	8.0	9.1	9.6	9.6	10.1

CONSTANT CONDITIONS	Cy., %	Temp., °C.	Retention time, Min.	pH range
Chlorination	3	Ambient	30	2.0-2.2
Alkali Extraction	5	60	60	10.6-10.8
Hypo I	10	42	90	7.0-7.5
Hypo II	10	33	60	7.5-8.0

Table 4.

Bleached Pulp Strength Properties
(Final slowness - 30°SR and Basis Weight - 60 ± 1 gsm)

Sequence Code / Particulars	A	B		C		D	
	CEHH	C_2EHH	C_3EHH	CEH_2H_2	CEH_3H_3	$C_2EH_2H_2$	$C_3EH_3H_3$
Beating time, Min.	11.0	12.0	12.0	12.0	12.5	12.5	13.0
Bulk, cm^3/g	1.52	1.50	1.49	1.48	1.48	1.43	1.43
Breaking length, Kms.	4.23	4.24	4.23	4.37	4.34	4.59	4.64
Stretch, %	3.5	3.5	3.5	3.6	3.7	3.6	3.7
Burst factor	41.3	42.3	42.4	43.3	43.3	44.8	45.3
Tear factor	83.5	84.7	84.8	80.0	84.6	85.3	87.5
Folding Endurance (MIT)	20	23	25	34	32	40	42
Strength index*	1650	1700	1710	1740	1770	1830	1860

* Strength index = $(B.F. \times T.F. \times \log DF)^{½} \times 100$

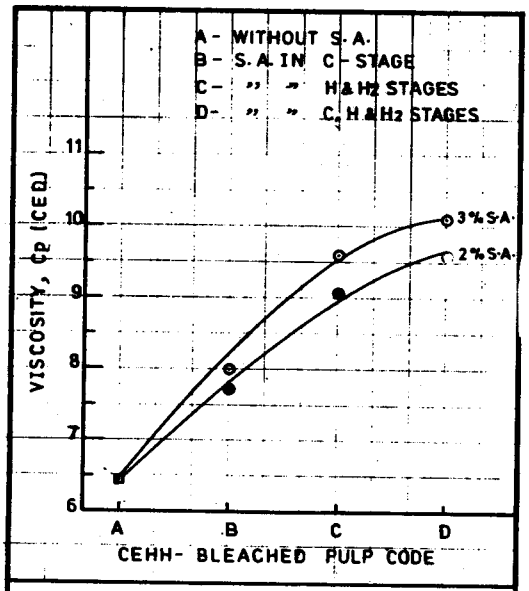

Fig.3: CHANGE IN BLEACHED PULP VISCOSITY WITH SULPHAMIC ACID

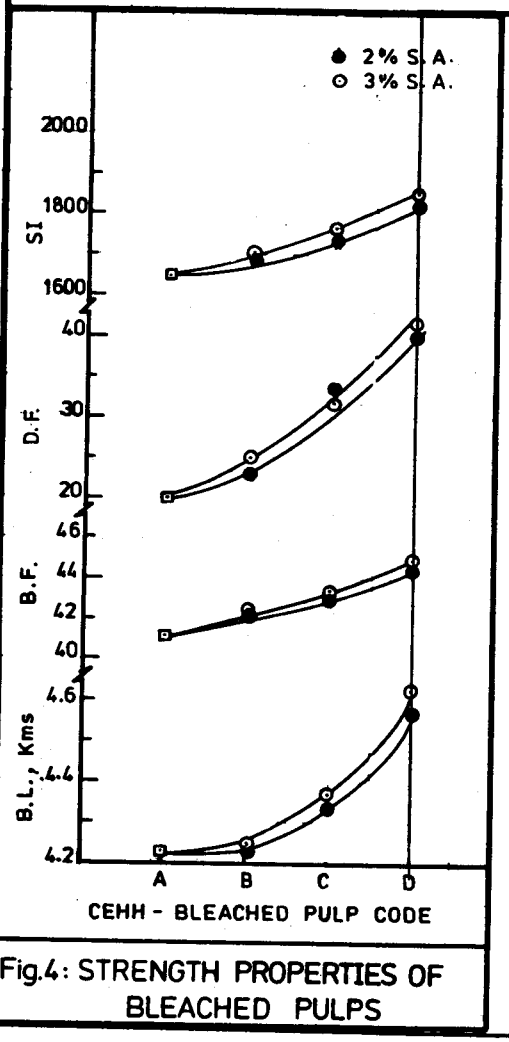

Fig.4: STRENGTH PROPERTIES OF BLEACHED PULPS

RESULTS AND DISCUSSIONS

As seen from Table No. I and Fig. 1, 2-3% sulphamic acid on available chlorine is found optimum as far as the viscosity is considered. After 3% addition of sulphamic acid, there is slight increase in the viscosity of bleached pulp. This trend is same whether the sulphamic acid is added in one, two or three stages of bleaching. The maximum benefit of viscosity development is observed when it is added in all 3 stages of bleaching i.e. chlorination and hypochlorite stages.

The similar trend is observed during the second set of experiments where 0-3% of sulphamic acid is added in various stages (Table No. II and Fig. 2). Upto 2% sulphamic acid addition, there is considerable improvement in viscosity, thereafter marginal development is observed.

The results of small scale bleaching experiments are confirmed by conducting large scale bleaching experiments (Table No. III and Fig. 3).

From Table No. IV and Fig. 4, it can be easily observed that there is definite improvement in overall strength properties when sulphamic acid is added in chlorination and both hypochlorite stages. Its addition in only chlorination stage did not improve the strength properties to the desired extent when compared to those in control bleaching experiment. When sulphamic acid was added in i) both hypochlorite stages, or ii) chlorination and hypochlorite stages, better development in paper strength was observed. Addition of sulphamic acid in all 3 stages - chlorination and hypochlorite stages yielded maximum strength development. There was hardly any difference in strength, when sulphamic acid dosage was increased from 2 to 3% in the concerned stages of bleaching. Hence only 2% sulphamic acid on available chlorine seems to be optimum amount of dosing.

CONCLUSIONS

1. A dose of 2-3% sulphamic acid in either the chlorination or hypochlorite stages is found to be optimum to achieve maximum improvement in bleached pulp viscosity.
2. Addition of sulphamic acid beyond 3% on available chlorine in chlorination and hypostages does not give any beneficial effect.

3. Maximum improvement in bleached pulp viscosity can be observed with the addition of 2% sulphamic acid in all stages i.e. chlorination and hypostages.
4. This has been confirmed by conducting large scale bleaching experiments.
5. Maximum improvement in strength characteristics of bleached pulps can be achieved with 2% addition of sulphamic acid in chlorination and hypochlorite stages.
6. Overall conclusion of this study is that sulphamic acid is a promising chemical in bleaching of pulp. Addition of 2% of sulphamic acid in solution form on available chlorine in chlorination and hypochlorite stages gives maximum improvement in pulp viscosity and strength characteristics.

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