Studies on the Degradation of Sulphate Pulps During Conventional Bleaching

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SUMMARY

For the raw materials bamboo, eucalyptus and mixed hardwoods, it was observed that the unbleached pulp viscosity had linear relationship with the Kappa Number, with a different slope for each raw material. It was noticed that at the same Kappa Number level, eucalyptus unbleached pulp showed highest viscosity followed by that of bamboo unbleached pulp which in turn was higher than the unbleached pulp viscosity of mixed hardwood pulp.

During bleaching of the unbleached pulps using C.E.H.H. sequence, the bulk of degradation was observed in chlorination and hypochlorite stages which was higher for bamboo pulps than eucalyptus or mixed hardwood pulps of the same Kappa Number level. The degradation was negligible during alkali extraction stage for all the three pulps.

Bamboo unbleached pulps of about 30 and 45 Kappa Numbers, on bleaching by C.E.H.H. sequence to a brightness level around 80% (Elrepho), using sulfamic acid as an additive in the hypochlorite stages showed total viscosity drops of 50% and 57% respectively based on the initial unbleached pulp viscosities. The eucalyptus unbleached pulps of similar Kappa Numbers showed total viscosity drops of 44% and 49% and for the mixed hardwood pulps the total viscosity drops were 34% and 43% respectively of their initial unbleached pulp viscosities. In all these experiments, 5% pulp consistency was used during the hypochlorite stages.

With the use of sulphamic acid and with 10% pulp consistency during the hypochlorite stages, the total drop in viscosity in C.E.H.H. sequence was about 10–15% higher as compared to the total viscosity drop in C.E.H.H. sequence, with 5% pulp consistency in the hypochlorite stages. With 10% pulp consistency for the hypochlorite stages, under similar bleaching conditions, increased brightness development of about 2–2.5 points was achieved.

INTRODUCTION

The objective of bleaching is to brighten the dark coloured unbleached pulp with minimum amount of chemicals and with minimum degradation and shrinkage of the cellulosic material. Thus, bleaching operation is said to be an extension of the delignification process, as the main undesirable component in the paper grade pulp is lignin.

In the multistage bleach plant of our mill, bleaching of the mixed pulp of bamboo and hardwoods is being done by the following sequence- Chlorination (C), Alkali Extraction (E), I Hypochlorite (H), and II Hypochlorite (H). Although elemental chlorine is a selective reagent, while reacting with lignin, there may be a degradation of cellulose and hemicelluloses, if the reaction is not controlled. Studies were carried out in Research Centre in the past with a view to optimise the conditions in the chlorination of bamboo and mixed hardwood pulps (1,2). As the chlorolignins formed during the chlorination stage are only partly soluble in hot water, the second stage of alkali extraction is carried out in which the remaining chlorolignins which are insoluble in hot water are dissolved in hot dilute sodium hydroxide solution. If the reaction during this stage is not controlled, degradation of pulp takes place. Studies were carried out in Research Centre in the past, and ideal conditions for this stage were recommended. It was also stated that the Kappa Number of pulp after optimum chlorination and alkali extraction should be between 7.0 and 8.5 (3). Further removal of the residual chlorine and brightening of the pulp

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is done by calcium hypochlorite. As compared to elemental chlorine, hypochlorite is not a very selective reagent and although the rate of attack on carbohydrates is much slower than on lignin, cellulose and hemicelluloses are damaged to some extent in hypo stages of bleaching. This damage depends on the pulp quality, concentration of chemicals, reaction time and temperature, and pH. Sulphamic acid is being used in our mill to minimise the pulp degradation during the two hypostages. It acts as a stabiliser for chlorine (4). This property has been utilised to minimise pulp degradation during hypo stages of bleaching in many mills the world over. It has been stated that the addition of 2–6% sulphamic acid based on available chlorine in either chlorination or hypochlorite stages would help to get final viscosity of bleached pulp, 25% higher than without it (5).

In addition to this, it takes care of the degradation due to increased temperature and pH values below 8. It is stated that 0.50 Kg/ton of sulphamic acid added during hypochlorite stage of a CEH sequence results in pulp which has equal brightness and reversion characteristics but 28% increase in pulp viscosity (6). The overall strength properties of the pulp in this particular instance, were better compared to that of the control. The trials carried out at the West Coast Paper Mills Ltd. using 0.1% sulphamic acid on pulp during hypochlorite stages, resulted in 36% increase in pulp viscosity with overall improvement in strength properties (7). All these results show the importance of sulphamic acid to minimise pulp degradation during hypochlorite stages of bleaching.

This work was undertaken to study the extent of pulp degradation during the different stages of a conventional bleaching sequence wherein sulphamic acid was used to minimise pulp degradation during the hypochlorite stages of bleaching.

EXPERIMENTAL

The raw materials used in the experimental work were collected from the mill raw material yard. Bamboos were chipped in the Pallmann chipper whereas eucalyptus and mixed hardwoods were chipped in the Voith chippers. The chips were air dried to attain 10–12% moisture.

The chips were screened in William's Chip Classifier and the results are recorded in Table 1. For the experimental work chips of -32 + 3 mm size were selected.

Pulping conditions were optimised in the electrically heated rotary laboratory autoclaves for these different raw materials. These were achieved by varying chemical dosage and also conditions like temperature and cooking time (H-factor). From bamboo, eucalyptus and hardwoods pulps of Kappa Numbers 25, 30, 35 and 45 were obtained using the optimum cooking conditions. The results are recorded in Table II. Also a plot of "H" factor

TABLE—I

DISTRIBUTION OF BAMBOO, EUCALYPTUS AND MIXED HARDWOOD CHIPS

Fraction, mm	%chips retained		
	Bamboo	Eucalyptus	Mixed hardwoods
+ 32	0.7	3.3	3.7
—32 + 25	4.6	7.6	8.0
—25 + 22	5.5	7.5	6.9
—22 + 19	9.7	11.6	9.8
—19 + 16	15.4	15.0	14.7
—16 + 13	16.5	16.1	16.4
—13 + 6	30.0	31.7	31.0
— 6 + 3	10.1	6.1	7.2
—3	7.5	1.1	2.3

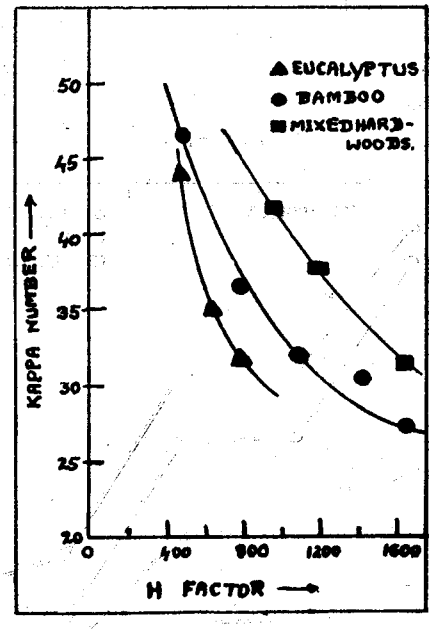

Fig. 1

vs. Kappa Number is given in Figure 1. All the unbleached pulp viscosities were determined following the standard Tappi procedure by giving sodium chlorite and acetic acid treatment. In Figure 2 Kappa Number vs. the unbleached pulp viscosity is plotted.

Bamboo, eucalyptus and mixed hardwood pulps of about 30 and 45 Kappa Numbers were bleached by C.E.H.H. sequence using optimum amount of bleaching chemicals and 5% pulp consistency in the hypochlorite stages. Sulphamic acid was used in hypo stages for protecting the pulp from deterioration. The bleaching conditions and the results are recorded in Table III. A set of bleaching experiments was also carried out using the above pulps of about 30 Kappa Number. Here, also sulphamic acid was used but 10% pulp consistency was maintained.

The bleaching conditions and the results are recorded in Table IV.

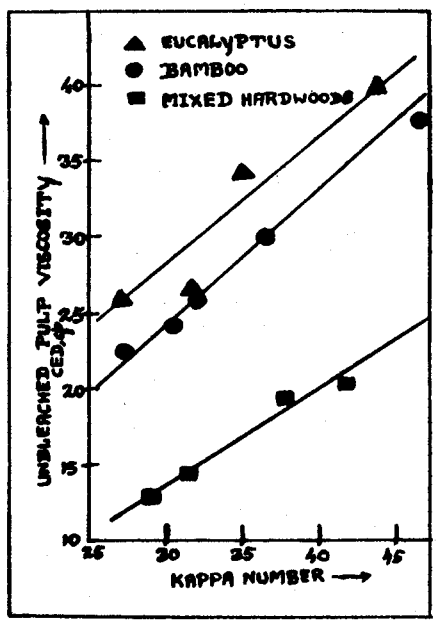

Fig.—II

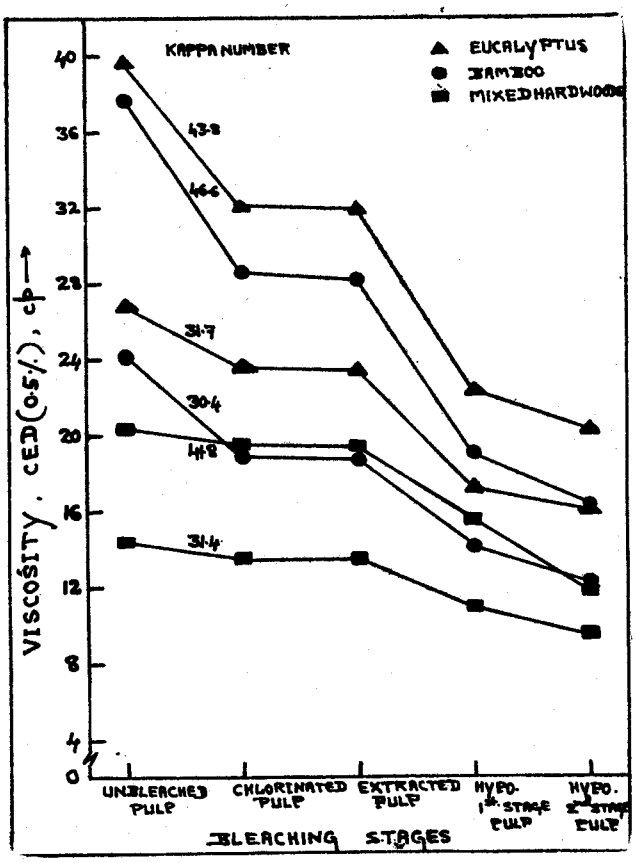

Fig.—III

The viscosity values determined at the different stages of the C.E.H.H. bleaching sequence of pulps of about 30 and 45 Kappa Numbers bleached with 5% pulp consistency in the hypochlorite stages and of the pulps of about 30 Kappa Numbers bleached with 10% pulp consistency in the hypochlorite stages have been recorded in Table IIIA and IVA respectively. These tables also give the percentage viscosity drop at different stages.

The viscosity values of the pulps of bamboo, eucalyptus and mixed hardwoods of about 30 and 45 Kappa Numbers determined at different stages of bleaching (with 5% pulp consistency in the hypochlorite stages) are plotted in Figure 3.

OBSERVATIONS AND DISCUSSIONS

For getting lower Kappa Number pulps delignification to a higher degree is to be done during pulping either by increasing chemicals or "H" factor or both. Hence, in the case of the lower Kappa Number pulps because of the severe conditions of pulping, the cellulose would be degraded to a greater extent compared to that of higher Kappa Number pulp. This has been clearly shown in Figure 2, wherein Kappa Numbers vs. the unbleached pulp viscosities are plotted. The graph also shows that, at nearly the same Kappa Number, the unbleached pulp viscosity of eucalyptus is highest, followed by bamboo unbleached pulp viscosity which was in turn higher than that of mixed hardwood pulp viscosity.

In the chlorination of eucalyptus and mixed hardwood pulps, the total chlorine applied (i.e. 1/6th of Kappa Number) was readily consumed and the pulp degradation was low as compared to the bamboo pulp degradation. In the case of eucalyptus pulps of about 30 and 45 Kappa Numbers, the drop in viscosity was 12% and 19%, whereas, in the case of mixed hardwood pulps it was 6% and 4% respectively. In the case of bamboo pulps the drop in viscosity was 22% and 24% respectively (Table IIIA). In the alkali extraction stages of all these pulps, under the experimental conditions stuidied, no noticeable degradation was observed.

In the case of bamboo pulps of about 30 and 45 Kappa Numbers, the total viscosity drop observed during bleaching (5% pulp consistency in hypochlorite stages) was about 50% and 57% respectively, of their initial unbleached pulp viscosities for about 80% brightness. In the case of eucalyptus and mixed hardwood pulps of nearly the same Kappa Numbers, the total viscosity drop observed during bleaching (5% cy. in hypo stages) was 44% and 49% for eucalyptus and 34% and 43% for mixed hardwood pulps respectively for about 80% brightness (Table-IIIA).

Bamboo, eucalyptus and mixed hardwood pulps of about 30 Kappa Numbers were bleached by CEHH bleaching sequence keeping 10% pulp consistency in the hypochlorite stages, the chlorine applied being the same as with 5% pulp consistency bleaching. The total drop in viscosity for the bamboo, eucalyptus and mixed hardwood pulps were 61%,

TABLE—II

PULPING* OF BAMBOO, EUCALYPTUS AND MIXED HARDWOOD CHIPS

Particulars	Bamboo					Eucalyptus				Mixed hardwoods			
Chemicals as Na_2O, %	17.0	17.0	17.0	17.0	17.0	16.0	15.0	15.0	15.0	20.0	18.5	18.5	18.5
Material :liquor ratio**	1:2.7	1:2.7	1:2.7	1:2.7	1:2.7	1:2.7	1:2.7	1:2.7	1:2.7	1:2.7	1:2.7	1:2.7	1:2.7
Cooking schedule :													
70°C. to max. temp., min.	90	90	90	90	90	90	90	90	90	90	90	90	90
At max. temp., min.	90	75	90	60	30	60	60	45	30	90	90	60	45
Max. temp., °C.	170	170	165	165	165	165	165	165	165	170	170	170	170
"H" factor	1640	1410	1090	780	480	780	780	630	480	1640	1640	1180	950
Results :													
Unbleached pulp yield, % (screened)	49.0	49.5	50.5	51.0	50.0	49.0	49.5	49.8	49.5	42.9	44.6	44.3	44.5
Rejects, %	1.2	1.5	0.8	2.2	4.0	0.3	0.6	0.4	1.1	0.4	0.4	1.5	1.6
Kappa Number	27.2	30.4	32.0	36.6	46.6	27.2	31.7	35.2	43.8	29.0	31.4	37.8	41.8
Black liquor at 17°Tw at 80°C.													
R.A.A.as Na_2O, gpl	8.0	8.7	9.3	10.2	12.6	7.8	5.9	6.5	6.8	10.5	7.4	10.9	11.1
Unbleached pulps :													
Viscosity*** (CED 0.5%), cp.	22.6	24.2	25.9	30.0	37.7	26.0	26.8	34.3	39.7	13.0	14.4	19.4	20.4

* The pulping experiments were carried out in the laboratory rotary digester.
** W.B.L. was used as a diluent.
*** Determined after the $NaClO_2$ treatment of the pulp as per the Tappi Standard.

TABLE–III

BLEACHING OF BAMBOO, EUCALYPTUS AND MIXED HARDWOOD SULPHATE PULPS

Particulars / Pulps	Bamboo		Eucalyptus		Mixed hardwood	
Unbleached pulp Kappa Number	30.4	46.6	31.7	43.8	31.4	41.8
Viscosity, cp.	24.2	37.7	26.8	39.7	14.4	20.4
Chlorination Stage :						
Chlorine added, %	7.60	11.70	5.50	7.50	5.50	7.20
Chlorine consumed, %	6.80	10.90	5.48	7.48	5.48	7.18
Alkali Extraction Stage :						
NaOH added, %	1.9	2.9	1.4	1.9	1.4	1.8
Final pH	9.0	9.7	8.3	8.3	8.6	8.3
Hypochlorite Ist Stage :						
Hypo added as av. Cl_2, %	2.50	3.00	1.75	2.00	2.50	2.75
Final pH	6.8	6.9	7.0	7.0	6.8	6.8
Hypo consumed as av. Cl_2, %	2.30	2.73	1.47	1.72	2.36	2.64
Pulp brightness, %	69.9	74.3	76.5	77.6	67.8	70.2
Hypochlorite 2nd Stage :						
Hypo added as av. Cl_2 %	1.00	1.00	0.50	0.50	1.20	1.50
Final pH	7.2	7.4	7.8	7.4	7.5	7.3
Hypo consumed as av. Cl_2, %	0.60	0.49	0.20	0.23	0.67	1.00
Total chlorine added, %	11.10	15.70	7.75	10.00	9.20	11.45
Total chlorine consumed, %	9.70	13.92	7.15	9.43	8.51	10.82
Brightness of bleached pulp, % (Elrepho)	78.8	80.8	80.4	81.6	77.8	79.6
Viscosity (CED 0.5%), cp	12.2	16.3	16.0	20.2	9.5	11.7

Constant Conditions :	C	E	H_1	H_2
Consistency, %	3	5	5	5
Temperature, °C.	Amb.	55±2	45±2	45±2
Time, Min.	60	60	60	90
Sulphamic acid on pulp, %	..	..	0.07	0.03

60% and 53% respectively of their initial unbleached pulp viscosities (Table—IVA).

CONCLUSION

(1) Higher Kappa Number pulps of bamboo, eucalyptus and mixed hardwoods showed higher unbleached pulp viscosities compared to the lower Kappa Number pulps. With severe pulping conditions and the lower the Kappa Number of the pulps, the degradation of the cellulosic material of the pulps was correspondingly more.

(2) At the same Kappa Number level, the eucalyptus pulps showed higher unbleached pulp viscosities compared to the bamboo pulp viscosities. However, the viscosities of mixed hardwood pulps were found to be the lowest, among those of the raw materials being used in our mills.

(3) **Bamboo pulps of 30.4 and 46.6 Kappa Numbers**

(a) During chlorination of these two pulps, the viscosity drops were 22% and 24% respectively of their unbleached pulp viscosities.

(b) During alkali extraction, further drop in viscosities were not observed.

(c) In the first hypochlorite stage, there was about 25 and 33% drop in viscosity (based on the alkali extraction stage viscosities); and the total viscosity drops observed in C.E. and H. stages were 42% and 50% respectively of their unbleached pulp viscosities.

(d) In the second hypochlorite stage, the viscosity drops were 13.5% and 14% (based on the 1st hypochlorite stage viscosities) respectively for the two pulps. In the C.E.H.H. bleaching to about 80% brightness, the total viscosity drops were 50% and 57% respectively, of their unbleached pulp viscosities.

(4) **Eucalyptus pulps of 31.7 and 43.8 Kappa Numbers**

(a) During chlorination of these two pulps, the viscosity drops were 12% and 19% respectively of their unbleached pulp viscosities.

(b) During alkali extraction no further appreciable drop in viscosities were observed.

(c) In the first hypochlorite stage, 27% and 30% drop in viscosities were observed (based on the alkali extraction stage viscosities) whereas, the total viscosity drops observed in C.E. and H stages were 36% and 44% respectively, of their unbleached pulp viscosities.

TABLE—IIIA

VISCOSITY DROPS DURING THE DIFFERENT STAGES OF BLEACHING

Particulars \ Pulps	Bamboo		Eucalyptus		Mixed hardwoods	
Unbleached pulps :						
Kappa Number	30.4	46.6	31.7	43.8	31.4	41.8
Viscosity* (CED 0.5%), cp.	24.2	37.7	26.8	39.7	14.4	20.4
Chlorinated pulps :						
Viscosity* (CED 0.5%), cp	18.8	28.6	23.6	32.0	13.5	19.5
Viscosity drop, %	22.3	24.2	11.9	19.4	6.2	4.4
Alkali Extracted pulps :						
Viscosity* (CED 0.5%), cp	18.7	28.2	23.4	31.9	13.5	19.4
Viscosity drop from C to E Stage, %	0.5	1.4	0.9	0.3	0	0.5
Total viscosity drop in C and E Stages, %	22.7	25.2	12.7	19.6	6.2	4.9
Hypochlorite Ist Stage pulps :						
Brightness of pulp, %	69.9	74.3	76.5	77.6	67.8	70.2
Viscosity (CED 0.5%), cp.	14.1	19.0	17.1	22.3	10.9	15.5
Viscosity drop from E to H stage, %	24.6	32.6	26.9	30.1	19.2	20.1
Total viscosity drop in CEH stages, %	41.7	49.6	36.2	43.8	24.3	24.0
Hypochlorite 2nd Stage pulps :						
Brightness of bleached pulp, % (Elrepho)	78.8	80.8	80.4	81.6	77.8	79.6
Viscosity (CED 0.5%), cp	12.2	16.3	16.0	20.2	9.5	11.7
Viscosity drop from H_1 to H_2 stage, %	13.5	14.2	6.4	9.4	12.8	24.5
Total viscosity drop in CEHH bleaching, %	49.6	56.8	44.0	49.2	34.0	42.6

*Viscosity was determined after the $NaClO_2$ treatment of the pulps.

Note—Viscosity drop at each stage has been calculated taking the previous stage viscosity as base whereas, the total drop at *each* stage is calculated on the basis of the unbleached pulp viscosity.

TABLE—IV

BLEACHING OF BAMBOO, EUCALYPTUS AND MIXED HARDWOOD SULFATE PULPS

Particulars	Pulps	Bamboo	Eucalyptus	Mixed hardwoods
Unbleached pulp Kappa Number		30.4	31.7	31.4
Chlorination Stage :				
Chlorine added, %		7.60	5.50	5.50
Chlorine consumed, %		6.80	5.48	5.48
Alkali Extraction Stage:				
NaOH added, %		1.9	1.4	1.4
Final pH		9.0	8.3	8.6
Hypochlorite Ist Stage :				
Hypo added as av. Cl_2, %		2.50	1.75	2.50
Final pH		7.0	7.1	6.9
Hypo consumed as av. Cl_2, %		2.38	1.59	2.41
Pulp brightness, %		74.9	79.5	71.6
Hypochlorite 2nd Stage :				
Hypo added as av. Cl_2, %		1.00	0.50	1.20
Final pH		7.0	7.3	7.0
Hypo consumed as av. Cl_2, %		0.74	0.35	0.89
Total chlorine added, %		11.10	7.75	9.20
Total chlorine consumed, %		9.92	7.42	8.78
Brightness of bleached pulp, % (Elrepho)		81.5	82.7	79.6
Viscosity (CED 0.5%), cp.		9.4	10.8	6.8
Constant Conditions				
	C	E	H_1	H_2
Consistency, %	3	5	10	10
Temperature, °C.	Amb.	55±2	45±2	45±2
Time, Min.	60	60	120	90
Sulphamic acid on pulp, %	..	..	0.07	0.03

TABLE—IVA

VISCOSITY DROPS DURING THE DIFFERENT STAGES OF BLEACHING

Particulars	Pulps	Bamboo	Eucalyptus	Mixed hardwoods
Unbleached pulps :				
Kappa Number		30.4	31.7	31.4
Viscosity* (CED 0.5%), cp		24.2	26.8	14.4
Chlorinated pulps :				
Viscosity* (CED 0.5%), cp.		18.8	23.6	13.5
Viscosity drop, %		22.3	11.9	6.2
Alkali Extracted pulps :				
Viscosity* (CED 0.5%), cp.		18.7	23.4	13.5
Viscosity drop from C to E stage, %		0.5	0.9	0
Total viscosity drop in C and E stages, %		22.7	12.7	6.2
Hypochlorite Ist Stage Pulps :				
Brightness of pulp, %		74.9	79.5	71.6
Viscosity (CED 0.5%), cp.		12.7	13.0	9.3
Viscosity drop from E to H_1 stage, %		32.1	44.5	31.1
Total viscosity drop in CEH stages, %		47.5	51.5	35.4
Hypochlorite 2nd Stage Pulps :				
Brightness of bleached pulp, % (Elrepho)		81.5	82.7	79.6
Viscosity (CED 0.5%), cp.		9.4	10.8	6.8
Viscosity drop from H_1 to H_2 stage, %		26.0	16.9	26.9
Total viscosity drop in CEHH bleaching, %		61.2	59.6	52.8

*Viscosity was determined after the $NaClO_2$ treatment of the pulps.

Note—Viscosity drop at each stage has been calculated taking the previous stage viscosity as base, whereas the total drop at each stage is calculated on the basis of the unbleached pulp viscosity.

(d) In the second hypochlorite stage, the viscosity drops were 6% and 9% (based on the 1st hypochlorite stage viscosities) respectively for the two pulps. In the C.E.H.H. bleaching to about 80% brightness, the total viscosity drops were 44% and 49% respectively of their unbleached pulp viscosities.

(5) **Mixed hardwood pulps of 31.4 and 41.8 Kappa numbers**

(a) During chlorination of these two pulps, the viscosity drops were 6% and 4% respectively of their unbleached pulp viscosities.

(b) During alkali extraction, further drops in viscosities was either zero or negligible.

(c) In the first hypochlorite stage, 19% and 20% drops in viscosities (based on the alkali extraction stage viscosities) were observed for these two pulps. The total viscosity drops observed in C.E. and H. stages were 24.3% and 24% respectively, of their unbleached pulp viscosities.

(d) In the second hypochlorite stage, the viscosity drops were about 13% and 24.5% (based on the 1st hypochlorite stage viscosities) respectively, for the two pulps. In the CEHH bleaching, to about 80% brightness, the total viscosity drops obtained were 34% and 43% respectively of their unbleached pulp viscosities.

(6) Using 10% pulp consistency bleaching in the hypochlorite stages, higher drop in viscosity was observed as compared to the total viscosity drop in CEHH sequence (with 5% pulp consistency in the hypochlorite stages), for all the three pulps, under the experimental conditions studied. With 10% pulp consistency bleaching (hypochlorite stages) there was about 2-2.5 points higher brightness develop ment achieved.

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