Stock Preparation Strategies- Part-II: Chelating on CEpHH and CEpHD Bleached Pulps

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ABSTRACT

A solution to the problem of brightness reduction on alum-rosin acid sizing in paper manufacturing, has been given through a new process of chelation, applicable to both CEpHH and CEpHD bleached pulps. Chlorine dioxide treated (CEpHD) bamboo- hard wood pulp is shown to possess properties different from pulp bleached in CEpHH sequence vis-a vis stock preparation. Effect of the chelating agent (EDTA) on chlorine dioxide bleached pulp has been studied in comparison with CEpHH-treated pulp. The sizing and other properties of the resultant pulps have been reported following to reverse sizing. The results have been used to throw light on the sizing mechanism. Brightness gain upto 6.0% El in CEpHD bleached pulp has been claimed with this new process.

INTRODUCTION

Chelating agents such as EDTA and DTPA have been employed in metal elimination (1-3) process for increasing bleaching efficiency of H_2O_2. This process will be of special significance when complete closure conception of paper mill will be practiced (4-7). Study employing chelating agents in stock preparation has probably not been carried out (8) as per our literature survey. As EDTA has chelating property over metal, it remains to be vividly ascribed its role in allowing anchoring of aluminium metals and simultaneously enhance the optical properties (8).

The dissociation constant (9) of EDTA-Fe and EDTA-Al are:

$$\text{Log K (EDTA - } Fe^{3+}) = 25$$

$$\text{Log K (EDTA - } Al^{3+}) = 24.$$

Complex with lower Log K value, namely Al^{3+} can thus replace Fe^{3+} easily. The replacement of Fe^{3+} (occurring in liquor) by Al^{3+} is thus facilitated more in reverse sizing as a result of which more of Fe^{3+} ions will be present in the liquor. It will contaminate the hand sheet and thus brightness will be lowered.

In ground wood pulp (10), brightness reduction upto 21.7 degree due to Fe^{3+} has been reported. Al^{3+} also reduces the brightness but to a lower degree than Fe^{3+} (-17^0). EDTA addition reduces this brightness drop if Fe^{3+} is >50 ppm (9).

Variations in stock preparation parameters between pulps bleached with different bleaching sequences, namely CEpHH and CEpHD were not considered important earlier. Rarely alteration in stock preparation strategy in the mill is also conceived while changing from CEpHH bleaching to CEpHD bleaching.

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EXPERIMENTAL

Bamboo-hard wood (70:30) mixed mill unbleached pulp has been collected from the nearby mill. CEpHH and CEpHD bleaching sequences have been followed to obtain the two sets of pulps. The bleaching characteristics of the pulps are given in **Table-1.** Pulps of 40^0 SR freeness have been prepared in Valley beater. These bleached pulps have been further treated with EDTA during stock preparation in normal and reverse sizing modes. 50 and 100 ppm of EDTA have been added to the stock. Alum and rosin have also been collected from the mill while a special grade talc from outside has been employed as filler (25% addition level). 1% of rosin has been added while 2.06 and 2.48% of alum have been employed, attaining the pH of ~ 4.5.

The bleaching characteristics including bleached pulp properties are shown in **Table-1.** The brightness of pulp bleached with CEpHH is 84.2% El while it is 88.2% El in CEpHD bleaching sequence. In terms of Cl_2 consumption, 0.65% more has been employed in case of later i.e. CEpHD sequence. With respect to OD pulp, the bleached pulp yield is reduced by 15.6% because of ClO_2 treatment compared to the pulp with CEpHH pulp. This reduction has been attributed to overall structural degradation of cellulose with removal of some surface -OH groups (11). It is logical to presume that this will bring in modification in sizing property.

In **Table-2,** the compositions of the stock solutions are given, namely alum in 2 concentrations, 2.06% and 2.48%, EDTA from 0 to 100 ppm and filler (talc) either 0 or 25%. Sets I and II contain pulps with CEpHH sequence while in III to VI, the pulps have been obtained through CEpHD bleaching sequence. Rosin has been fixed to 1% in all the sets. Experiments have been conducted either in normal sizing or reverse sizing where the sequence of addition has been as follows:

Normal Sizing (N)		Reverse Sizing (R)
EDTA	Step-I	EDTA
Rosin	Step-II	Alum
Alum	Step-III	Rosin
Filler	Step-IV	Filler

Same water has been used in all the experiments. In the sets I and II, the alum concentration has been fixed to 2.06% while in III and IV, it was to be changed to 2.48% as the chlorine dioxide treated pulp is apparently less acidic. pH of 4.5 being the target, it has been varied from 4.45 to 4.62 in the sets. In sets V and VI, however 2.06% of alum has benn taken for comparison with pulps with CEpHH bleaching. The filler addition level has been fixed to 25% as in earlier experiment (12, 13), it was found to impart the optimum sizing, retention and scattering coefficient values. EDTA has been added 50 or 100 ppm as similar concentrations have been used in metal elimination process (2, 3).

RESULTS AND DISCUSSION

The cobb, ash content and drainage time of the pulps bleached with CEpHH and CEpHD sequences are given in **Table-3.** The cobb value which determines essentially the sizing efficiency is found to have some unusual results, specially in chlorine dioxide based pulp having EDTA treatment (VI). Cobb values of 72.9 g/m^2 have been obtained with reverse sizing mode while in normal sizing the value is 42 g/m^2. Set IV have the cobb value of 22.5 g/m^2, while in normal sizing the value is 20.1 g/m^2, which is lower than others with ClO_2 bleached pulps. On the other hand, the CEpHH- bleached pulp having EDTA treatment (100 ppm) has the cobb value of 17.9 g/m^2 at 25% of filler addition level. Thus the pulp having undergone ClO_2 sequence, presents inferior sizing efficiency compared to that with CEpHH sequence. Marginal increase in cobb value of ODED-bleached pulp compared to CEpHH bleached bagasse pulp has been reported (14) attributing the increase to higher α-cellulose content. The high increase of cobb value in EDTA treated pulp is due to metal elimination (3) including aluminium.

The ash contents of ClO_2-bleached pulps are higher than those in pulp with CEpHH bleaching. It becomes obvious if comparison is made between I (12.1%) and V (12.8%) for filled paper and between II (9.9%) and VI (11.5%) sets for EDTA treated pulps. The fine content in chlorine dioxide bleached pulp has been reported to be higher than without ClO_2 treatment and the fibre fines having higher surface area can adsorb alum as well as filler to

Table-1

Bleaching characteristics of bamboo-hardwood mixed pulp:

Particulars		**CEpHH**	**CEpHD**
Moisture	(%)	68.33	68.33
Kappa no.		17.00	17.00
CHLORINATION :			
Cl_2 added	(%)	4.1	4.1
Cl_2 consumed	(%)	3.90	3.91
Final pH		2.19	2.20
ALKALI EXTRACTION :			
NaOH added	(%)	1.37	1.37
Final pH		10.09	9.00
HYPO-I STAGE :			
Hypo (available Cl_2) added	(%)	2.19	2.74
Buffer added	(%)	0.4	0.4
Final pH		7.38	7.36
Cl_2 (as available) consumed	(%)	1.80	2.16
HYPO-II / ClO_2 STAGE :		**HYPO-II**	**ClO_2**
Hypo/ClO_2 (available Cl_2) added	(%)	0.55	0.50
Final pH		10.00	4.34
Cl_2 (as available) consumed	(%)	0.16	0.44
Total chlorine applied	(%)	6.84	7.34
Total chlorine consumed	(%)	5.86	6.51
Bleached Yield	(%)	94.7	79.1
Shrinkage	(%)	5.3	20.9
Brightness	(% El)	84.2	88.2

Constant conditions:	**Chlorination**	**Extraction**	**Hypo Stage**		**ClO_2 stage**
			I	**II**	
Temperature (°C)	35	55	35	35	70
Retention time (hr)	0.75	1.5	3.0	1.0	3.0
Consistancy (%)	3.0	10	10	10	10

Table-2						
Composition and pH of different sets studied						
Set No.	**Alum (%)**	**Chelating agent (ppm)**	**Filler addition (%)**	**pH**	**Mode of addition**	**Bleaching sequence**
I	2.06	0	25	4.45	R	CEpHH
II	2.06	100	25	4.62	R	CEpHH
III	2.48	0	25	4.54	R	CEpHD
IV	2.48	100	25	4.47	R	CEpHD
V	2.06	0	25	4.66	R	CEpHD
VI	2.06	100	25	4.61	R	CEpHD

increased level (15, 16). The EDTA treatment causes reduction in ash content as it can be compared between I (12.1%) and II (9.9%) and between V (12.8%) and VI (11.5%). This finding can be correlated with again elimination of metals because of chelation effect.This reduction has been observed in both the pulps i.e. pulp with CEpHH bleaching and CEpHD bleaching. However, the decrease is more (2.2%) in CEpHH-bleached pulp than in CEpHD pulp (1.3%).

The fact that EDTA brings in reduction in filler retention can be found to be valid with increased alum content (2.48% in stead of 2.06% above) also; in III, the ash content is 13.5% while in IV, it is 13% both being in reverse sizing. In case of normal sizing and at alum 2.06% addition, the filler retention property between CEpHH and CEpHD pulp is not different as the values of 11.6% and 11.9% respectively obtained in presence of EDTA (100 ppm) and 25% filler addition. As in normal sizing alum is added after rosin, EDTA addition induces chelation effect for Al^{3+} of alum to a lesser degree; in this case Al^{3+} apparently complexes with rosin first and EDTA can not compete with Al-rosin complex. However with CEpHH pulp where alum addition percentage is 2.48 and in normal sizing mode, the ash contents in EDTA treatment at 50 and 100 ppm are on the higher side i.e. 13.0% and 12.5% respectively.

(a) Pulp - EDTA - Alum - Rosin.....(R)

(b) Pulp - EDTA - Rosin - Alum.....(N).

The situations can be envisioned as above on effect of alum addition in normal sizing and reverse sizing modes on sizing and filler retention proper-

Table-3			
Cobb, ash and drainage time of hand sheets			
Set No.	**Cobb (g/m²)**	**Ash content (%)**	**Drainage time (sec)**
I	16.5	12.1	23.5
II	17.9	9.9	12.17
III	19.1	13.5	59.96
IV	22.5	13.0	50.70
V	21.9	12.8	58.50
VI	72.9	11.5	56.51

Table-4				
Optical properties of hand sheets				
Set No.	**Brightness (% El)**	**Opacity (%)**	**Yellowness (%)**	**Scattering coefficient (m^2 /kg)**
I	70.3	92.0	15.2	41.78
II	71.1	91.8	14.1	41.06
III	66.5	94.3	17.5	45.11
IV	72.5	90.6	14.9	42.59
V	74.9	90.7	13.3	45.68
VI	73.0	92.9	14.4	41.29

ties. In the normal sizing , EDTA has to compete with rosin for its reaction with alum while in reverse sizing alum reacts immediately with EDTA, after which even if rosin is added, it can not break the Al-EDTA complex. Formation of this complex does not contribute for filler rather it causes reduction in filler retention properly and the sizing efficiency also deteriorates.

The results of drainage property in **Table-3** are of importance also as the drainage time in CEpHD pulps are much higher (50-60 sec) than in CEpHH pulps (12-23.5 sec). Here again the higher values can be attributed to presence of higher proportions of fines due to ClO_2 bleaching stage. The effect of EDTA addition on drainage property is also significant for both the CEpHH and CEpHD bleached pulps.

The optical properties such as brightness, opacity, yellowness and scattering coefficient values of hand sheets subjected to both CEpHH and CEpHD sequences are presented in **Table-4**. The set nos. II and IV have been treated with EDTA and the brightness values have been observed to be higher i.e. 71.1% El and 72.5% El respectively than set I (70.3% El) and set III (66.5% El). Similarly the higher brightness of 73.6% El and 74.8% El are also obtained in normal sizing at alum 2.06% and 2.48% respectively with ClO_2 treated pulp in presence of EDTA (100 ppm). With CEpHH pulp in normal sizing with EDTA addition of 0, 50 and 100 ppm, the brightness values are 68.9, 72.7 and 71.1% El respectively. Thus EDTA treatment, normally attributable for sequestering of metal ions, brings improvement in brightness properties.

The opacity values of ClO_2 - treated pulps are not much different from the CEpHH-treated pulps. The EDTA-treatment does not help in improvement of opacity. The yellowness (%) of pulps treated with ClO_2 is marginally lowered for CEpHH and CEpHD treated pulps at alum addition of 2.06% and 2.48% respectively.

The scattering coefficient values have also increased in pulps treated with CEpHD bleaching sequence compared to CEpHH-bleached pulps. EDTA addition has also marginal effect. The highest values of 45.68 m^2/kg and 45.11 m^2/kg observed in sets V and III respectively have the common reverse sizing mode but with alum variation of 2.06 and 2.48%.

The surface properties, namely smoothness and porosity are presented in **Table-5** for CEpHH and CEpHD bleached pulps. The smoothness values marginally increase while the porosity values have decreased in the CEpHD pulps compared to CEpHH pulps. The difference in porosity values between CEpHH and CEpHD pulps are fairly substantial and it may be inferred that ClO_2-treatment improves the porosity which may be because of higher fine contents (17). The fines occupy the voids and the porosity value decreases (16).

Table-5

Surface properties of hand sheets

Set No.	Smoothness (ml/min)	Porosity (ml/min)
I	95	270
II	105	310
III	110	180
IV	105	170
V	115	160
VI	115	150

Comparison of strength properties in hand sheets with CEpHH and CEpHD pulps can be made between the sets I-II and III-VI in **Table-6.** The bulk value decreases marginally due to ClO_2 - treatment i.e. from ~1.5 cc/g in CEpHH to ~1.4 cc/g in CEpHD bleaching. Little changes in tear factor, burst factor, breaking length and double fold are observed on adding ClO_2 bleaching sequence. Treatment of EDTA has also no adverse effect here.

The chelating process in stock preparation will thus be applicable to pulps having bleached both by CEpHH and CEpHD sequences. The flow diagram for the total process is shown in **Fig.1.**

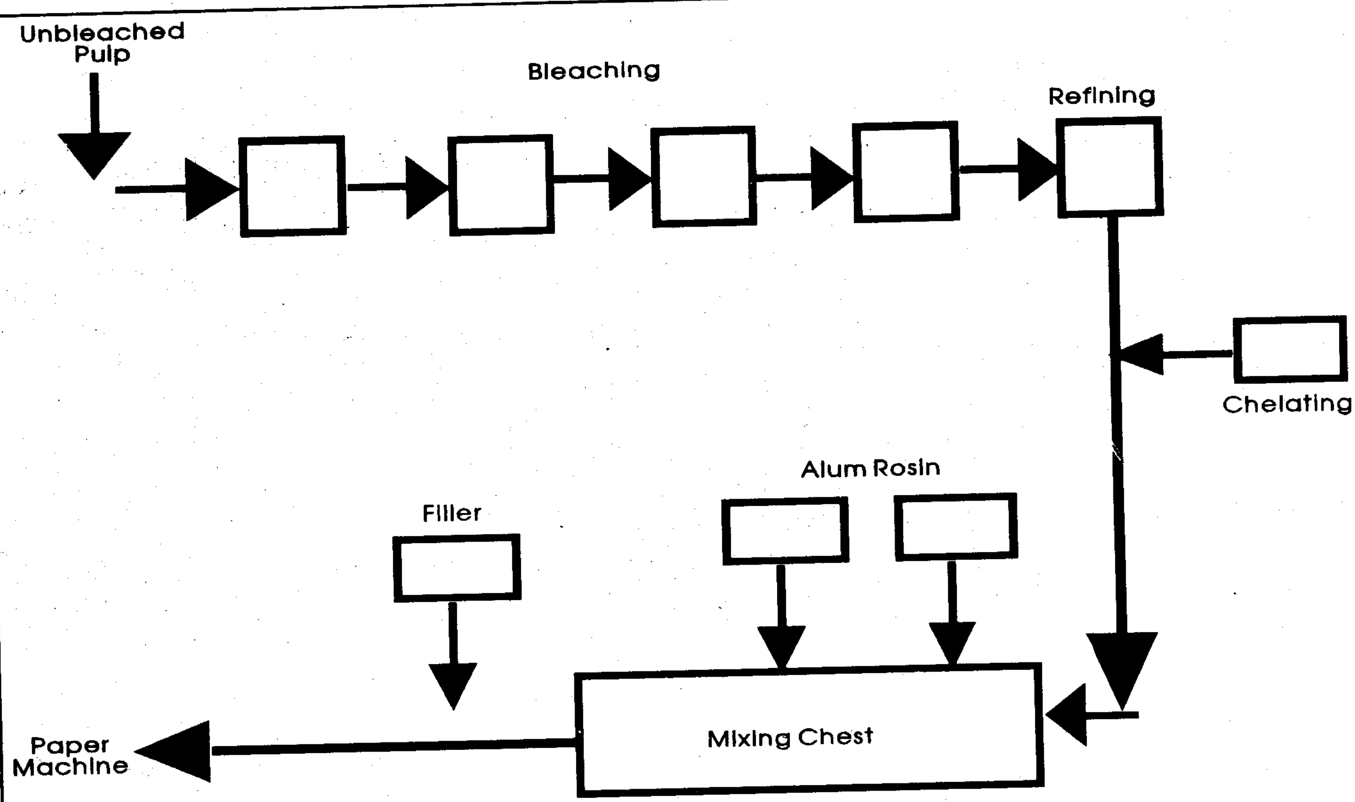

Fig.1: Sizing with chelating process

Table-6

Strength properties of hand sheets

Set No.	Bulk (cc/g)	Tear factor	Burst factor	Breaking length (m)	Double fold (no)
I	1.46	59.1	34.3	5960	26
II	1.49	65.3	34.3	5860	24
III	1.41	58.0	31.2	5555	28
IV	1.39	58.4	35.4	6060	26
V	1.39	60.0	32.3	5575	20
VI	1.43	60.4	34.8	5570	20

Chelating stage in the stock preparation may be more beneficial when hard water or water with less purity, as the case may be in rainy season, will be used by the mill. The chronic problem of reduction in stock brightness due to rosin and alum thus can be eliminated on chelation. However, this new process should be tried separately in other raw materials or water before applying in the mill scale.

CONCLUSIONS

The brightness gain in CEpHH pulp due to addition of EDTA here is found to be 3.8% El (in normal sizing with EDTA addition of 0 and 50 ppm) and in CEpHD pulp, the btightness gain is 6.0% El (set III and IV). According to the results obtained the conditions for maximum brightness gain with acceptable sizing property for CEpHH and CEpHD pulps are recommended to be as follows :

	Sizing mode	Alume dose (%)	pH	Rosin (%)	EDTA (ppm)	Talc (%)	Brightness gain (% El)
CEpHH	N	2.06	4.59	1	50	25	3.8
CEpHD	R	2.48	4.47	1	100	25	6.0

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