Role of Hydrogen Peroxide in Further Brightness Enhancement of Chemical Pulp in "Chlorine Dioxide And Oxygen" Bleaching

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INTRODUCTION

During the last 10-15 years Indian Pulp and Paper Industry is gradually shifting from traditional CEHH bleaching technique to innovative bleaching techniques suitable for Indian raw material as well as acceptable to Indian economy. In mid eighties CEHD bleaching sequence was introduced in some of the mills in India. It was, however, not operative in many of the mills then. This could be either due to fear psychosis on safe generation/usage of chlorine dioxide or due to high cost of manufacture of bleached writing printing grade pulp. Around same time the advantage of alkalinity as well as temperature at alkali extraction stage in CEHH bleaching sequence was exploited and hydrogen peroxide was introduced at alkali extraction stage (1-3). Thus this dead time and heat energy at extraction stage were utilised to carry out bleaching of pulp. This bleaching technique has become popular and is being practiced for bamboo, hardwood as well as on nonwood fibres in India by many pulp and paper mills. This CEpHH bleaching sequence has helped the paper industry.

1. to improve the brightness of pulp at final stage
2. to reduce the colour of extraction wash liquor
3. to reduce the consumption of hypochlorite at subsequent hypochlorite bleaching stages which can reduce the AOX generation as well reduce the post colour reversion of pulp.

There was also a school of thought that by usage of chlorine dioxide at final stage of CEHD/CEHHD bleaching sequence one can go higher up on brightness. This was also one of the reasons for many paper mills to set-up chlorine dioxide plants. However, due to limitation of hypochlorite for brightening of pulp and its detrimental effect on mechanical properties of fibres, it was diffcult to achieve the goal of brightness. Hence, there was a need to modify these bleaching sequences.

The advent of oxygen bleaching technique in India in mid nineties of last millennium, some of the financially sound paper mills set-up captive oxygen plants and started usage of oxygen. Some of the mills discarded the usage of hydrogen peroxide and switched over to either CEHD or CE_OHD bleaching sequences. However, by end nineties mills faced pressure from market for paper with higher brightness as well as from statutory bodies to be a good neighbour for reducing pollution load including reduction in AOX/ TOCL. At the same time, paper industry was passing through global competition at one end and the domestic financial crunch at other end. Hence, no mill was in a position to invest in modification of pulping/ bleaching section by incurring any capital expenditure. Therefore, some alternatives were considered.

It is well known that CEHD bleaching sequence alone cannot take the brightness of pulp to higher level i.e. beyond 85°ISO without sacrificing the mechanical properties of pulp. Hence, there should be sufficient brightness at H stage to increase it further. This is achievable by usage of hydrogen peroxide at alkali extraction stage in CEHD bleaching sequence (4-8). Similarly in case of CE_OHD bleaching technique oxygen's benefits can be extended further by adding hydrogen peroxide to E_O stage, a process known as E_{OP}. Using H_2O_2 alongwith with O_2 gives synergical effect of bleaching to improve brightness, lower chlorinated extraction (CE) Kappa number for pulp and reduce chlorinated effluent (9).

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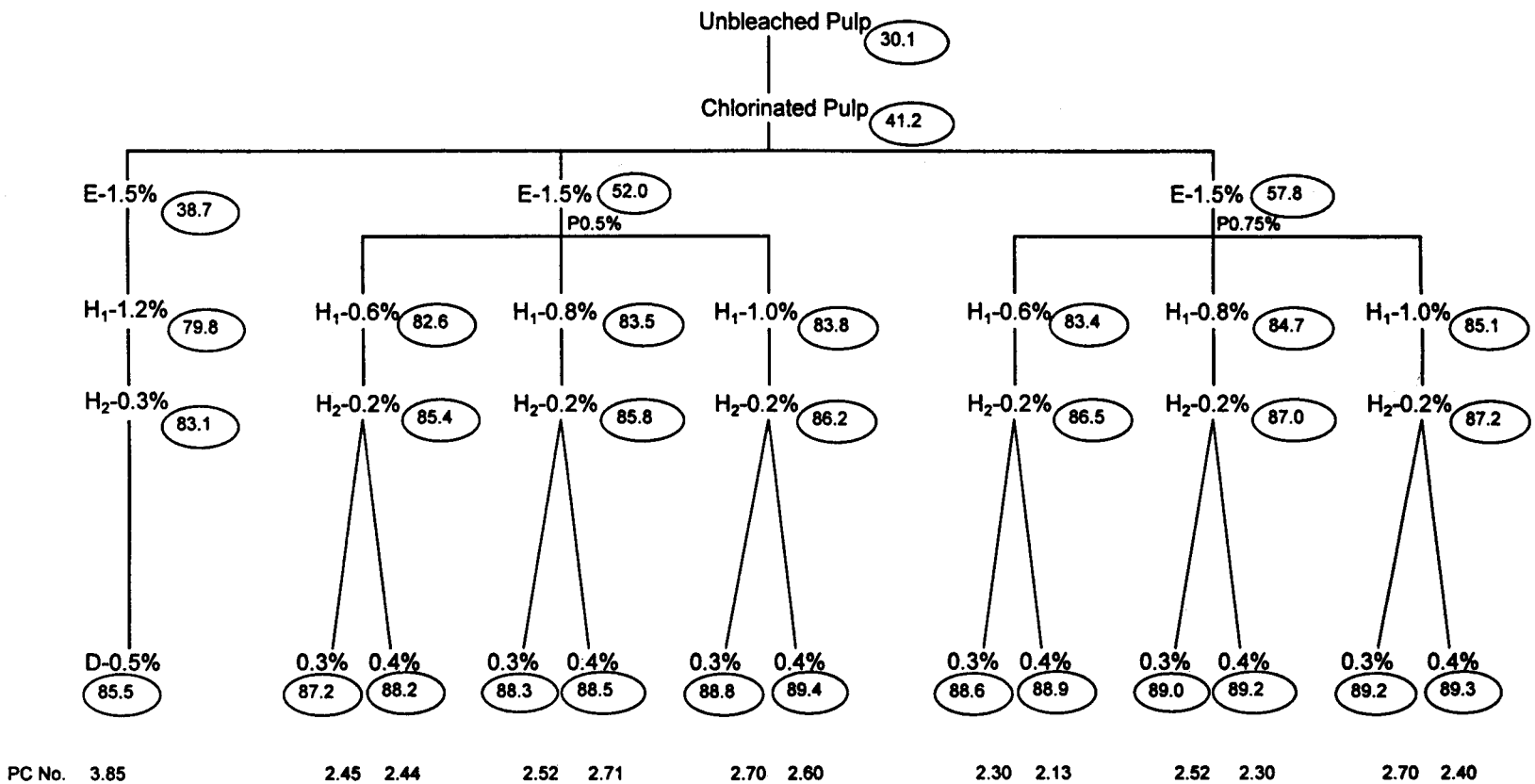
TABLE-1 BLEACHING CONDITIONS OF VARIOUS PLUP SAMPLES.(IN GENERAL)

		1A					1B				1C				1D						
	RAW MATERIAL	HARDWOOD + BAMBOO					HARDWOOD+BAMBOO				BAGASSE				HARDWOOD PULP (RAYON GRADE)						
	BLEACHING SEQUENCE	C_DEHHD					CE_OHD				C_DE_ODA				CEHEDHA						
	PARAMETERS	CD	E	H	H	D	C	E_O	H	D	CD	E_O	D	A	C	E	H	E	D	H	A
											3				2						
1	CHLORINE (A.C)% ON O.D. PULP	3.0					6.5														
												2.2				2		0.5			
2	CAUSTIC - DO -		1.5					3.0													
																	0.7			0.3	
3	HYPOCHLORITE - DO -			1.2	0.3				2.5												
4	HYDROGEN PEROXIDE - DO -																				
													0.4						0.4		
5	CHLORINE DIOXIDE - DO -	0.2				0.5				0.5											
														0.2							0.18
6	H_2SO_4 - DO -																				
												3									
7	OXYGEN kg/cm^2								3.0												
											3.5	10	10	10	2.5	10	10	10	10	10	10
8	CONSISTENCY	5.3	10	10	10	10	3	10	10	10											
											AMB	70	80	AMB	AMB	65	60	65	80	60	45
9	TEMPERATURE °C	AMB	65	38	38	70	AMB	65	40	70											
											60	120	240	30	45	90	120	90	150	120	45
10	RETENTION TIME (MIN)	45	90	90	150	180	45	30+60	180	180	60	120	240	30	45	90	120	90	150	120	45

Fig.1 : C_DEHD & C_DE_PHD Bleaching of Hardwood Bamboo Chemical Pulp.



1 ⬭ - Brightness Values are °ISO
2 Chemical Charge is on O.D. Pulp
3 H2O2 Dosage on 100% basis (P)

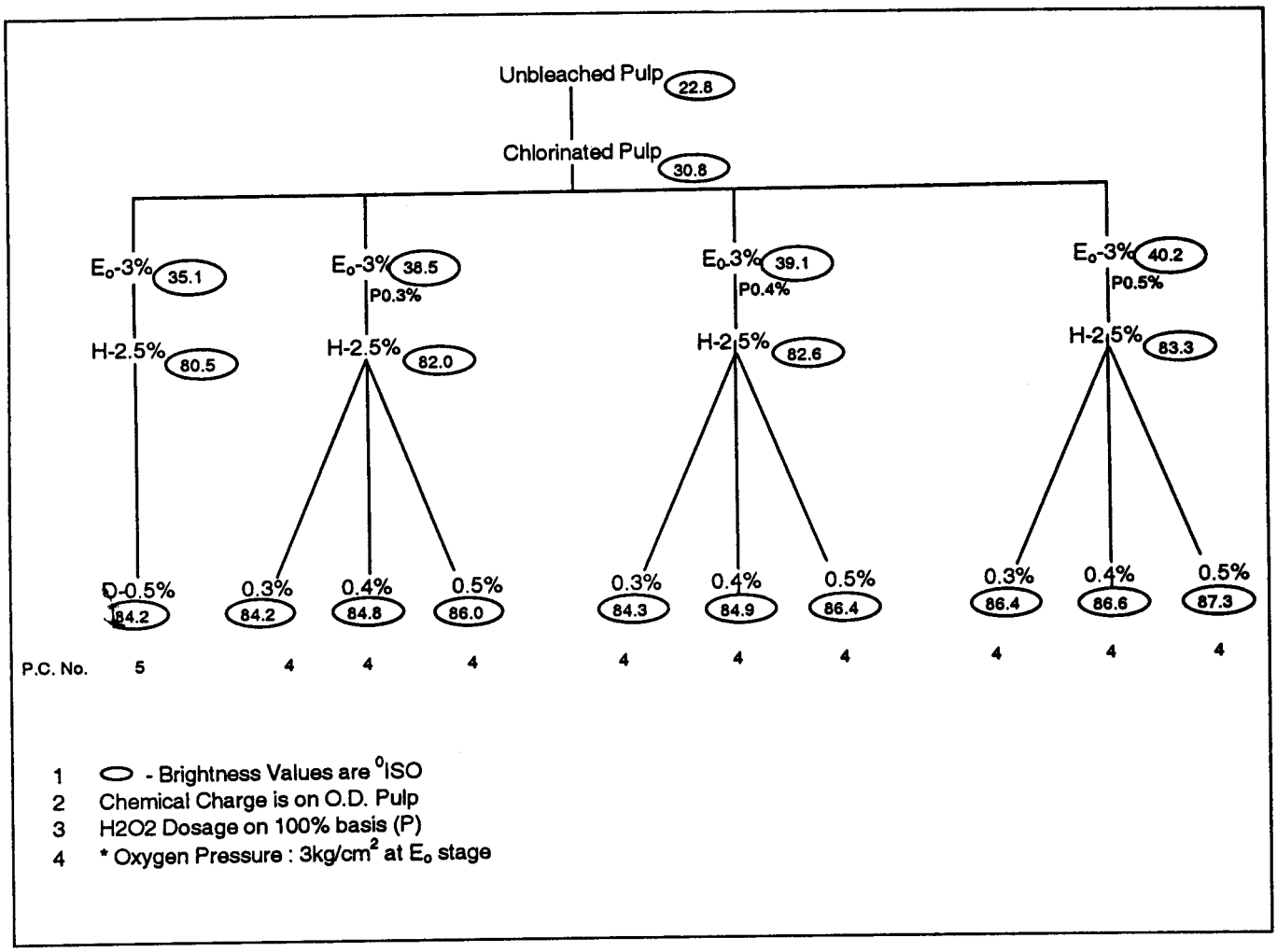


Fig. 2 : CE_oHD & $CE_{OP}HD$ Bleaching of Hardwood Bamboo Chemical Pulp.

During the tenure of this study efforts have been made to use hydrogen peroxide at extraction stage of CEHD/ CE_oHD bleaching techniques and modify these sequences into CE_PHD/$CE_{OP}HD$ bleaching sequences. The efforts have also been made to study the effect of H_2O_2 on final brightness as well as on consumption of chlorine dioxide during bleaching. The unbleached pulp samples were collected from paper mills of repute and comparative study was carried out on:

1. C_DEHD & C_DE_PHD bleaching sequences for hardwood pulp.
2. CE_oHD & $CE_{OP}HD$ bleaching sequences for hardwood pulp.
3. C_DE_oD & $C_DE_{OP}D$ bleaching sequences for bagasse pulp.
1. CEHEDH & CE_PHEDH bleaching for dissolving grade hardwood pulp.

CHEMISTRY OF PEROXIDE BLEACHING

Earlier efforts have been made to explain chemistry of P as well as (O+P) at extraction stage (2, 10, 11). In this paper, therefore, the explaination on chemistry of hydrogen peroxide has been avoided.

EXPERIMENTAL

In all above cases the study was initiated from unbleached pulp samples collected from some large paper mills. The unbleached pulp was disintegrated in laboratory disintegrator and dewatered on 200 mesh. This pulp after determining consistency was subjected for bleaching treatment in polyethylene bags as per bleaching stages given in bleaching sequence in

laboratory water bath. Chlorination, alkali extraction, hypochlorite bleaching were carried out by simulating plant conditions as per parameters given in Table-1. Oxidative extraction of pulp was carried out in laboratory model rotary digester. 3.0 kg./cm^2 pressure was maintained with retention of about 30 minutes at 65°C in digester. The oxygen pressure was released after 30 minutes and alkali extraction either with or without peroxide stage was further continued for one hour. The general bleaching conditions for various pulp samples are given in Table-1a to 1d.

Brightness values were measured as °ISO on Technibrite TB 1C instrument from Technidyne USA.

A bench scale study has also been undertaken for dissolving grade pulp. The brightness as well as cuprammonium viscosity values have been determined at each of the bleaching stages of dissolving pulp.

OBSERVATIONS AND DISCUSSIONS

Fig-1 shows that brightness of C_DEHHD bleached hardwood pulp was 85.5 °ISO. The same was elevated to 88-89 °ISO by usage of 0.5 to 0.75% H_2O_2 (100%) on O.D. pulp at extraction stage. Thus the rise in brightness was of the order of 3-4 units which is really remarkable.

It has been also observed that there was a reduction of 5 kg. hypochlorite and 2 kg. chlorine dioxide per tonne of pulp by usage by 5 kg. H_2O_2 (100%) per tonne of pulp at alkali extraction stage. Even with such reduction brightness of final pulp was elevated atleast by 3-4 units.

The reduction in consumption of hypochlorite has helped to improve the brightness stability of pulp. This has been indicated by lower P.C. reversion values. This is absolutely evident that usage of hydrogen peroxide at extraction stage improves the brightness stability of chemical pulp as against any other chlorine based chemical used for bleaching.

Fig. 2 shows that the brightness of CE_OHD bleaching sequence is 84.2° ISO. However by introducing 0.3 to 0.5% H_2O_2 (100%) on pulp at alkali extraction stage has helped to increase the brightness further upto 87.3° ISO i.e. raising almost by 3 units. In all the cases whenever hydrogen peroxide is used at extraction stage alongwith oxygen the final brightness has gone up showing synergical effect of oxygen and hydrogen peroxide.

Even the usage of 0.3% H_2O_2 (100%) at extraction without reducing chlorine dioxide at final stage the brightness value can be elevated by almost 2° ISO. It has been also observed that by addition of 3 kg. H_2O_2 (100%) per tonne of pulp at extraction it is possible to reduce almost 2 kg. chlorine dioxide consumption per tonne of pulp.

TABLE-2 BRIGHTNESS °ISO OF DISSOLVING PULP AT VARIOUS BLEACHING STAGES P-H_2O_2 (100%) AT FIRST 'E' STAGE.

BLEACHING STAGE	C	E	H	E	D	A
BLANK	55	65	79	81	85	86
P 0.3%	55	74	82	83	86	88
P- 0.4%	55	78	83	84	88	90

TABLE-3 VISCOSITY VALUES OF DISSOLVING PULP AT VARIOUS BLEACHING STAGES P-H_2O_2 (100%) AT FIRST 'E' STAGE.

BLEACHING STAGE	C	E	H	E	D	A
BLANK	17.1	15.1	11.7	10.7	9.9	9.8
P 0.3%	16.6	14.7	12.7	12.0	11.2	10.5
P- 0.4%	17.6	14.0	11.6	11.5	10.7	10.7

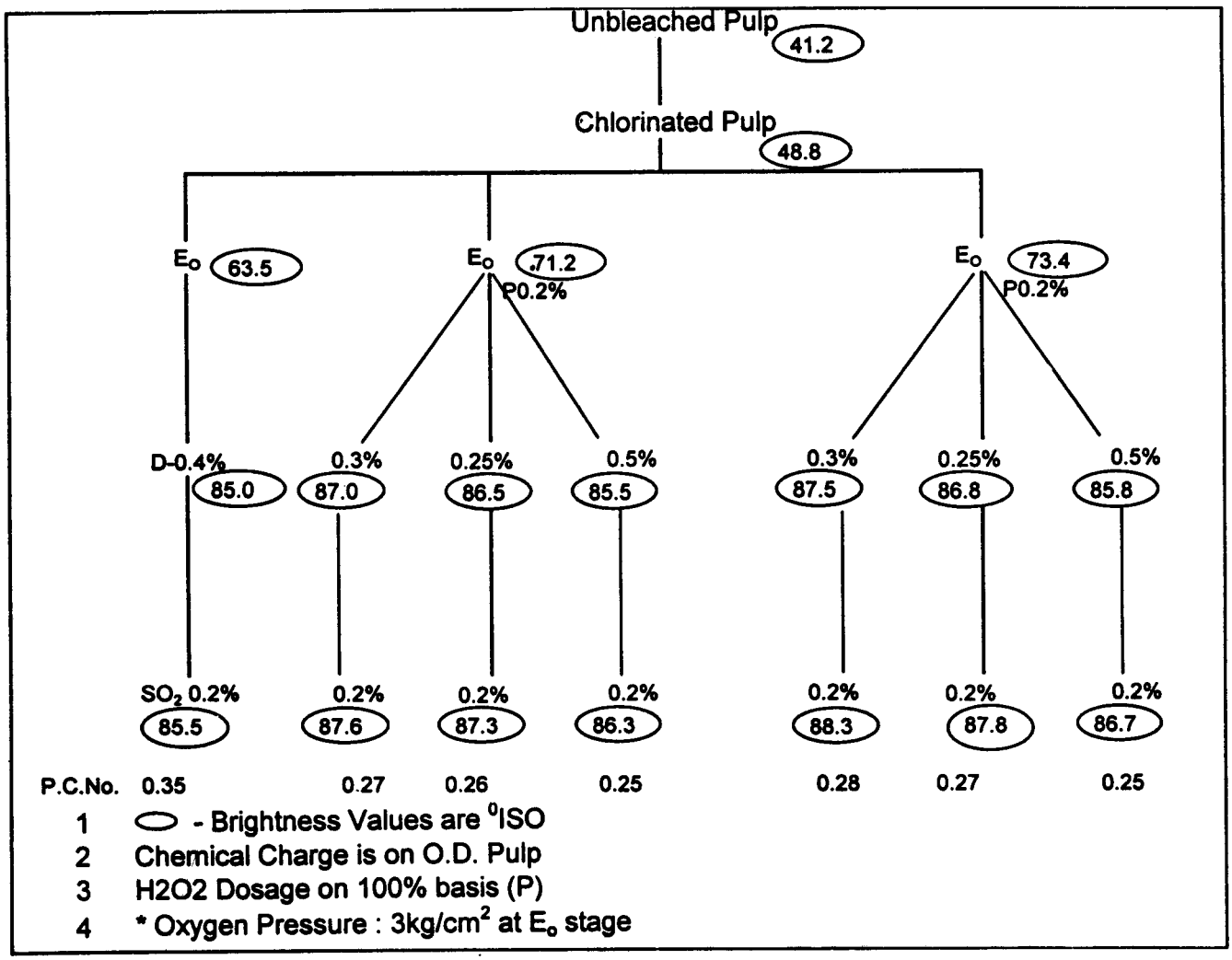


Fig. 3 : C_DE_OD & $C_DE_{OP}D$ Bleaching of Bagasse Chemical Pulp.

In case of nonwood fibre pulp i.e. Bagasse chemical pulp with C_DE_OD bleaching sequence it has been observed that by usage of 2 kg. H_2O_2 (100%) per tonne of O.D. pulp at extraction stage, one can not only save 2 kg. chlorine dioxide per tonne of pulp but also can elevate the brightness by 1° ISO i.e. from 85.5° to 86.8° ISO. It has been also observed that one may elevate brightness of the pulp further to 88° ISO by usage of 3 kg. H_2O_2 (100%) per tonne of pulp but also by saving 1 kg. Chlorine dioxide.

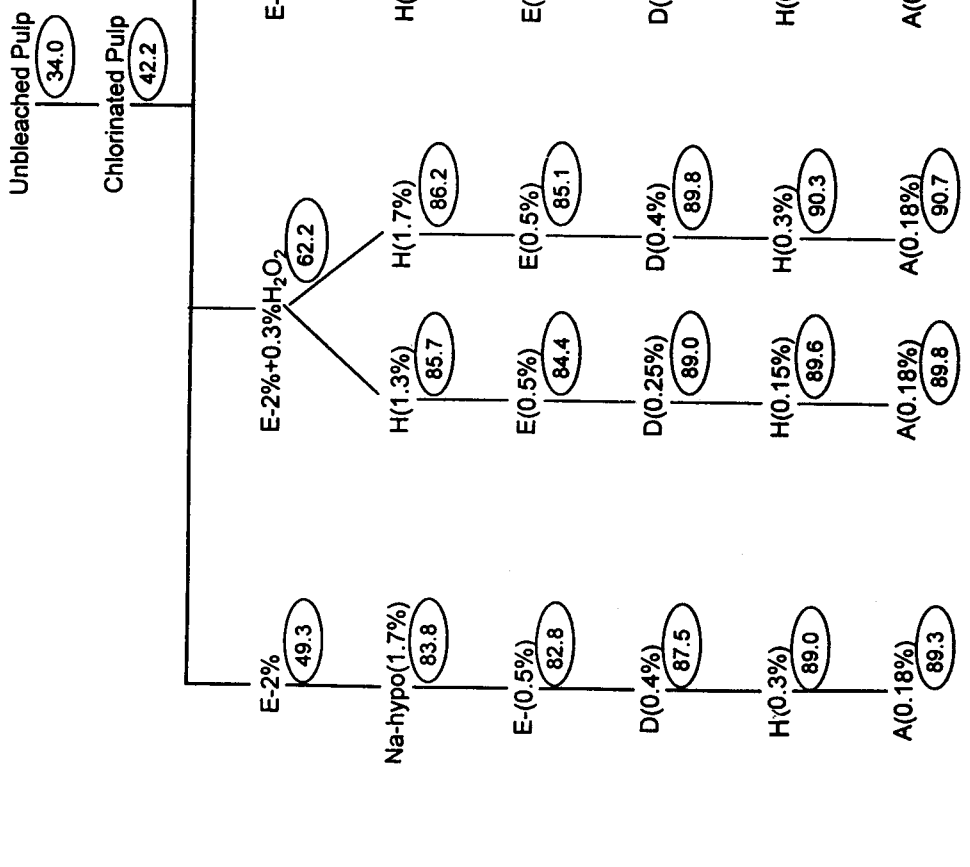
TABLE-1d gives the bleaching conditions with CEHEDH bleaching sequence for dissolving pulp. Here Sodium hypochlorite is being used at hypochlorite stage. Second stage hypochlorite's job is to correct viscosity of dissolving pulp. This is one of the requirements of dissolving pulp.

Fig. 4 shows that by usage of 3 kg H_2O_2 (100%) per ton of O.D. pulp at extraction stage one can reduce 1.5 kg. of chlorine dioxide to achieve same brightness level. But in case higher brightness is required it is possible to do so without reducing chlorine dioxide consumption.

Similar results were obtained by usage of 0.4% and 0.5% H_2O_2 (100%) at alkali extraction stage.

Fig.5 & 6 show brightness and viscosity values of pulp respectively at various stages of bleaching sequence of dissolving pulp. With increase in peroxide dosage, the brightness values of pulp increase gradually (Fig.-5). Similarly viscosity values are also controlled although peroxide is being used at extraction stage. (Fig.-6). But in actual practice one has to strike a balance between usage of hydrogen peroxide and chlorine dioxide tohave desired viscosity of fully bleached dissolving pulp for further

Fig. 4 : CEHEDH & CE_pHEDHD Bleaching of Dissolving Pulp of Hardwood.



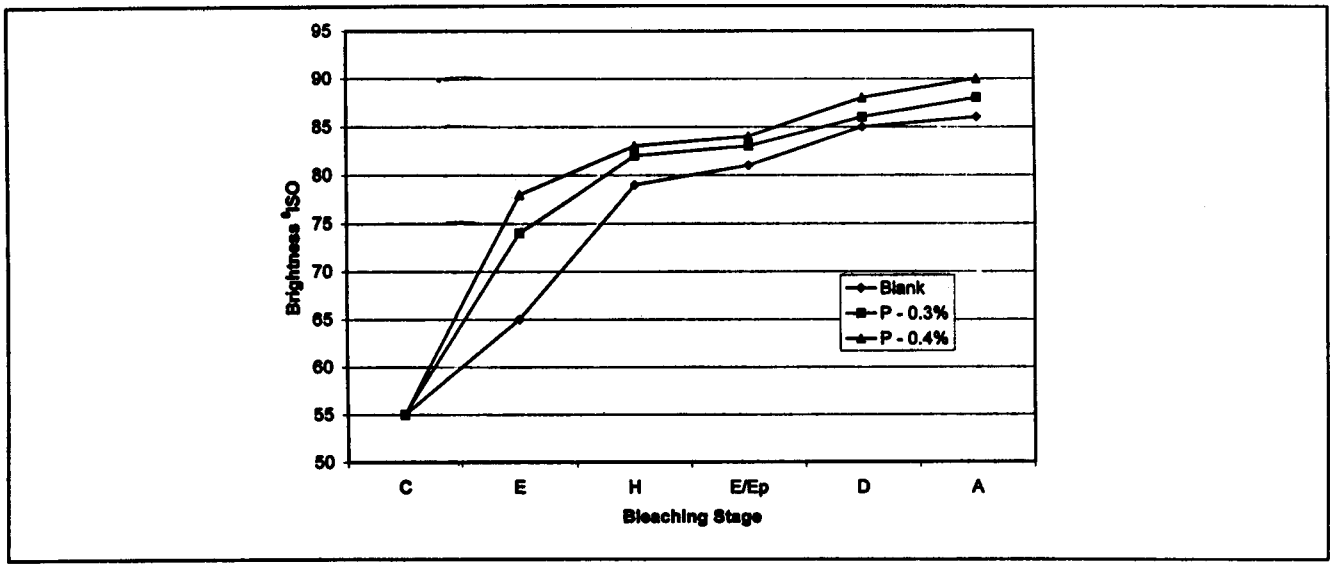


Fig. 5 : Brightness (°ISO) at Various Bleaching Stages for Dissolving Grade Pulp.

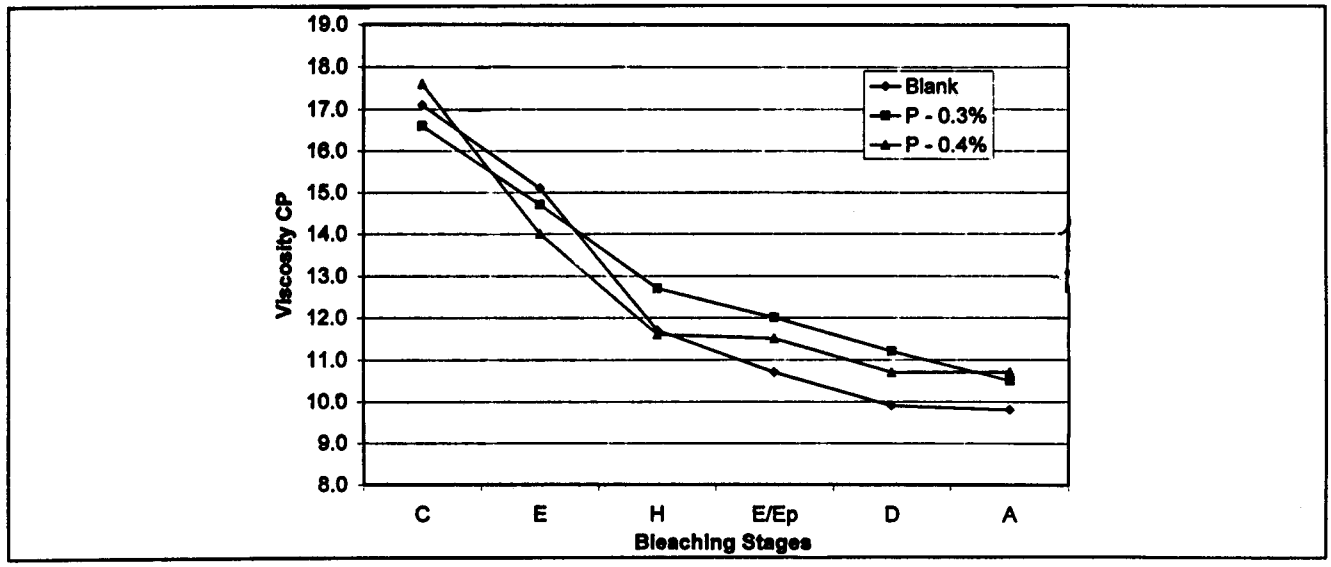


Fig. 6 : Viscosity (CP) at Various Bleaching Stages for Dissolving Grade Pulp.

processing.

CONCLUSIONS

Brightness of chemical pulp bleached by sequence having oxygen and chlorine dioxide can be further improved by usage of small dosage of hydrogen peroxide at extraction stage. Thus oxygen, chlorine dioxide do not compete with hydrogen peroxide but all these bleaching chemicals act to complement the bleaching process.

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