

# High Consistency Hydrogen Peroxide Bleaching Of Hardwood Chemimechanical Pulp

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## ABSTRACT

*Hydrogen peroxide is lignin preserving bleaching chemical used mainly for bleaching of mechanical pulps. At Hindustan Newsprint Ltd., hardwood chemimechanical pulp is bleached with hydrogen peroxide at medium consistency of 10%. To produce high brightness newsprint, chemimechanical pulp with high brightness is required in the furnish. To achieve high brightness (65% Elrepho) for the chemimechanical pulp at medium consistency, the peroxide requirement is high which becomes uneconomical due to the higher cost of hydrogen peroxide. High brightness mechanical pulp can be produced more economically with hydrogen peroxide bleaching at high consistency.*

*In the present study, the peroxide bleaching of hardwood chemimechanical pulp was carried out at high consistency (20%) and the results are compared with medium consistency (10%) bleaching results. Bleaching of coloured filtrate present with the unbleached CMP was also studied to assess the hydrogen peroxide consumed by the unbleached filtrate during the hydrogen peroxide bleaching. By increasing the consistency from 10% to 20%, the hydrogen peroxide requirement for bleaching can be reduced from 5.5% to 3.5% which amounts to a saving of 20 Kg hydrogen peroxide per MT of pulp.*

*Based on the above results HNL is embarking to high consistency Hydrogen Peroxide bleaching of CMP. This will enable to produce Newsprint of high brightness to meet the international competition.*

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## INTRODUCTION

Hydrogen Peroxide is an environment friendly bleaching chemical widely used in paper industry, especially for the bleaching of mechanical and chemimechanical pulps to attain high brightness with least yield loss. Bleaching of mechanical pulp (SGW) with hydrogen peroxide was first commercially adopted by St. Regis Paper Co., U.K. in 1941. Soft wood unbleached mechanical pulps in general have brightness varying between 55-65%. These pulps with 2-3% Hydrogen perox-

ide gain brightness ranging from 10-18 units (1). In comparison to this the brightness of hard wood unbleached chemimechanical pulps vary between 25-35% and these can be bleached to 55-58% brightness with 2-3% hydrogen peroxide for using in newsprint furnish. The brightness of

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newsprint made from such furnish should be of at least 65%. For bleaching hardwood CMP to 65% brightness, the requirement of peroxide at medium consistency is high which becomes uneconomical due to high cost of hydrogen peroxide. It is due to this reason that the brightness of newsprint produced from hard wood chemimechanical pulp is limited to 55%.

There are a number of variables other than process conditions which affect the brightness response of the pulps during hydrogen peroxide bleaching. The bleaching response of certain mechanical pulps from some soft wood species to hydrogen peroxide bleaching depends upon the presence of extractives. Mechanical pulps from hard wood species show considerable variation in their response to hydrogen peroxide bleaching. The superiority of Birch over Aspen chemimechanical pulps with respect to hydrogen peroxide bleachability has been reported by Fiala et al and by Blackburn et al. Age of the tree has been reported to have a bearing on the brightness attained due to the chemical changes occurring in the heart wood fraction with age (2).

Bark impurities have been found to have a negative effect in the bleaching of spruce TMP and CTMP. Decay in wood may also adversely affect the hydrogen peroxide bleaching response by virtue of enzymes present (eg. catalase) which catalyse the hydrogen peroxide decomposition (2). The transition metals in wood also contribute to the poor peroxide bleaching response of the pulps.

The process variables which affect the bleaching response in hydrogen peroxide bleaching are pH, alkalinity, temperature and consistency. The brightness response of mechanical and chemimechanical pulps to hydrogen peroxide is enhanced by increasing the pulp consistency in bleaching (2). Pilot plant studies and commercial operations indicated a substantial improvement in the bleach response to an eastern coniferous wood pulp as a result of increasing consistency from 12% to 25% (3). Spruce/Fir TMP bleached at 30% consistency in plant trials attained the same brightness with half the peroxide and alkali consumption as at 12-20% consistency in optimised laboratory bleaching experiments (2). At high consistency, higher concentration of bleach-

ing chemical is maintained with the fibre and is available for bleaching. Moreover, a larger concentration gradient is obtained between the bleaching chemical and fibre (4). High consistency bleaching amounts to less carry over of the unwashed spent liquor to the bleaching process resulting in lower requirement of bleach chemical to the extent being consumed by such spent liquor. Because of all these reasons high consistency bleaching often results in significantly lower levels of  $H_2O_2$  requirement. More significant results with high consistency hydrogen peroxide bleaching have been observed for difficult to bleach pulps such as highly sulfonated pulps (CMP)

## **CHEMIMECHANICAL PULPING PROCESS AT HNL**

In the chemimechanical pulp mill, the alkali impregnated hard wood chips are refined in two stages in series in RL-58 Raffinators. The unbleached pulp after Raffinator-II is washed on a single stage drum washer and sent for bleaching.

The bleaching plant was originally designed for 2 stage calcium hypochlorite bleaching. The calcium hypochlorite and caustic were added at the unbleach washer repulper which pass through a mixer before falling into a downward flow bleach tower at 10% consistency. After a retention time of about 100 minutes in the tower the pulp is diluted to about 3.5% consistency and additional quantity of hypo and caustic as required were added before pumping into the upflow second retention tower which gave a retention time of about 40 minutes. The pulp from the second bleach tower over flowing at the launder was washed over the bleach washer. The washed pulp was refined in the third raffinator from where it falls into a stock chest. From this stock chest the pulp was processed in centricleaner and centrifugal screens and thickened before sending to high density tower for storage.

## **HYDROGEN PEROXIDE BLEACHING OF CHEMIMECHANICAL PULP**

HNL switched over to medium consistency, single stage hydrogen peroxide bleaching in 1989. The existing calcium hypochlorite bleaching system

as such was utilised for Hydrogen Peroxide bleaching. The bleaching chemicals (Hydrogen Peroxide, Soup solution consisting of caustic and sodium silicate, and Magnesium sulphate) are added at the repulper of the unbleach washer. The Hydrogen Peroxide charge varies depending upon the type of hard wood in the raw material mix. The requirement of other chemicals remain more or less similar. The initial pH is maintained at 10.3-10.5 and the temperature is maintained at 75°C with LP steam given at the mixer. Retention time of 100 minutes is provided in the downward flow tower (Bleach Tower-1) at 10% consistency. The pulp in the Bleach Tower-1 is diluted at the ring at the bottom with bleach washer filtrate to 3.5% consistency and pumped to the second retention tower which provides 40 minutes retention time. No bleach chemicals are added in this stage. The peroxide left over at the end of first stage retention and from the bleach filtrate introduced through the ring dilution react with the pulp in the Bleach tower-2 increasing the brightness by about 2 units. The existing bleaching system adopted for hydrogen peroxide bleaching of CMP at HNL is shown in Fig.1.

The replacement of calcium hypochlorite bleaching with medium consistency hydrogen peroxide bleaching has considerably reduced the pitch deposits, reduced the ash content in bleached pulp due to elimination of calcium soaps, improved saveall performance at paper machine with better machine runnability and productivity. Though environmental aspects were not the major consideration in adopting hydrogen peroxide bleaching, it has helped in reducing the environmental pollution by eliminating the formation of chlorinated organic compounds (AOX) and also reducing the BOD and COD load in the discharges. In short, the use of hydrogen peroxide for the bleaching of chemimechanical pulp has helped in maintaining the system clean. However as the existing old bleaching system was used with hydrogen peroxide also, the pulp consistency in bleaching had to be maintained at 10%. About 25-30 kg of hydrogen peroxide was required per tonne of bleached pulp to achieve a brightness of 55-57%. The brightness of newsprint with this chemimechanical pulp in the furnish was in the range of 53-55%.

To meet the international competition in the quality of newsprint, HNL decided to improve the brightness of its newsprint to 60-62%. To achieve this target the brightness of chemimechanical pulp at 20% consistency to achieve the above target economically. The results are compared with the medium consistency bleaching.

The carry over of the unbleached filtrate along with the pulp plays an important role in the bleaching and the final bleached pulp brightness in the case of hydrogen peroxide bleaching. One of the reasons for lower requirement of hydrogen peroxide in high consistency bleaching is due to the lower amount of unbleached filtrate carried with the pulp when the consistency is increased. To assess the savings in hydrogen peroxide consumption due to this, separate experiments were carried out to bleach the unbleached filtrate (removal of the color) with hydrogen peroxide under similar conditions of pulp bleaching and the amount of hydrogen peroxide required was determined.

#### EXPERIMENTAL

The unbleached chemimechanical pulp from chemimechanical pulp mill was used for the bleaching experiments. The pulp was produced from a mixture of hard woods having a composition of 35.5% Eucalyptus hybrid from Karnataka region, 30.5% Acacia auriculaeformis, 33.0% Eucalyptus globulus and 1.0% Murikku (*Erythrina Varigata*). The age of the wood was 4 years for Karnataka hybrid, 7 years for Acacia auriculaeformis, 14 years for Eucalyptus globulus and 10 years for Murikku. The pulp was produced with 6% caustic impregnation of chips and two stage refining in Sunds RL-58 Raffinators in the chemimechanical pulp plant.

Hydrogen peroxide bleaching was carried out at 20% consistency (high consistency) and 10% consistency (Medium consistency). For bleaching at 20% consistency, the unbleached pulp was dewatered in a centrifuge to about 25% consistency. For bleaching at 10% consistency, unbleached pulp as such from the unbleach washer having 14% consistency was taken. 1.5% sodium silicate (38°Be), 0.03% magnesium sulphate and caustic as required to maintain the pH were added to the pulp, mixed well and then different doses of hydrogen peroxide

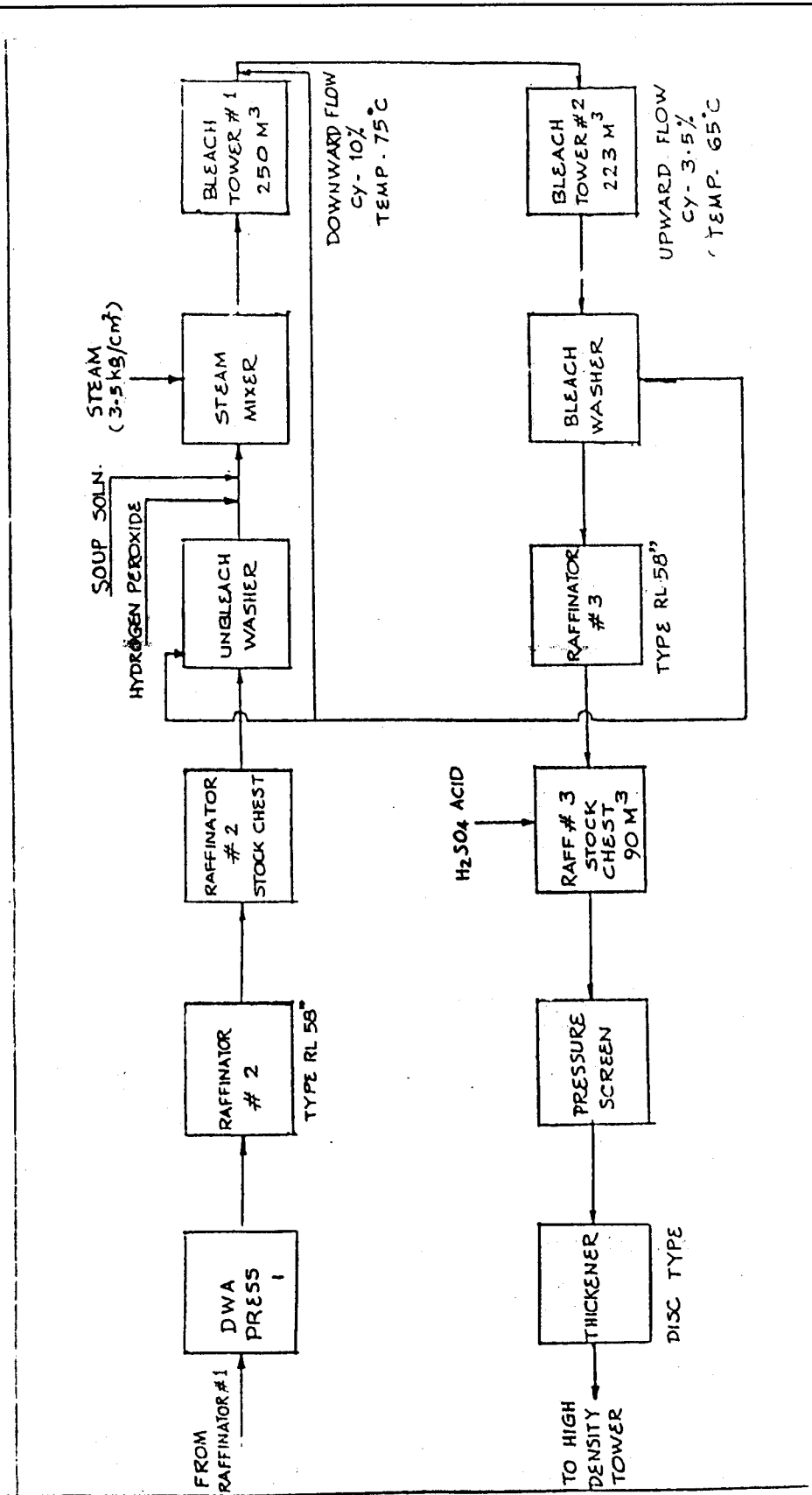


Fig.1. Block Diagram Of Existing Hydrogen Peroxide Bleaching System Of Chemi-Mechanical Pulp AT HNL

TABLE-1

## HYDROGEN PEROXIDE BLEACHING OF UNBLEACHED CHEMIMECHANICAL PULP

Sl. No.	Particulars Consistency	Unit	Results										
			10%					20%					
1.	Unbleached pulp brightness	%	36.3										
2.	Peroxide as H <sub>2</sub> O <sub>2</sub> (100%)	%	3.0	4.0	5.0	6.0	7.0	3.0	3.5	4.0	4.5	5.0	5.5
3.	Alkali as NaOH	%	1.44	1.55	1.73	1.90	2.06	1.44	1.50	1.57	1.65	1.73	1.81
4.	Sodium Silicate (38 <sup>0</sup> Be)	%	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
5.	Magnesium Sulphate	%	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
6.	Initial pH	-	10.7	10.7	10.7	10.7	10.7	10.7	10.7	10.7	10.7	10.7	10.7
7.	Final pH	-	9.7	9.7	9.6	9.6	9.7	9.7	9.6	9.6	9.6	9.6	9.7
8.	Residual Peroxide (100%)	%	0.78	1.14	1.32	1.65	1.87	0.75	0.84	0.98	1.17	1.31	1.43
9.	Peroxide Consumed	%	2.22	2.86	3.68	4.35	5.13	2.25	2.66	3.02	3.33	3.69	4.07
10.	Bleached pulp brightness	%	60.2	61.7	64.1	65.6	66.4	63.3	64.8	66.5	67.5	68.3	68.9
<u>Constant conditions</u>			<u>Peroxide stage</u>										
a) consistency %			10.0/20.0										
b) Temperature °C			75										
c) Retention Minutes			120										

varying from 3.0% to 7.0% were added. The initial pH was maintained at 10.7 with caustic solution. A temperature of 75°C and a retention period of 2 hours were maintained during bleaching. The bleaching was carried out in plastic bags and the temperature was maintained in a water bath.

The chelating agents like DTPA, EDTA etc are well known for their efficient complexing of the transition metals to prevent the catalytic decomposition of peroxide during hydrogen peroxide bleaching. However, during the optimisation of conditions in peroxide bleaching of hard wood chemimechanical pulp, the pretreatment of pulp with DTPA has shown only a marginal improvement in brightness. Hence, the sequestering chemical was not used in the bleaching experiments. The ineffectiveness of DTPA may be probably due to the inactivation of metal ions by colloidal magnesium silicate which is formed from the reaction between Magnesium sulphate and sodium silicate during peroxide bleaching. After completion of bleaching, the final pH and the residual hydrogen peroxide were tested. The pulps were diluted to 3% consistency and acidified with dilute sulphuric acid to 5.5 pH. Brightness

sheets were made, air-dried and tested for brightness. The bleaching conditions and the results are given in Table-I. The pulp brightness at different additions of hydrogen peroxide and the peroxide consumed are plotted in Figure-2.

#### PEROXIDE BLEACHING OF UNBLEACHED PULP FILTRATE

The unbleached chemimechanical pulp contains coloured filtrate. The coloured filtrate in the pulp consumes some peroxide for decolourisation during peroxide bleaching to get a final colour equivalent to the colour of bleach washer filtrate.

To the unbleached pulp filtrate, 0.25% sodium silicate (38<sup>0</sup>Be), 0.005% Magnesium sulphate and different doses of peroxide ranging from 0.05% to 0.175% (equivalent to 0.30% to 1.07% dose on pulp at 14% consistency) and 0.04% caustic to maintain 10.2 pH were added. A temperature of 75°C was maintained and 2 hours reaction time was given. At the end of the reaction time, the residual colour was tested. The reaction conditions and the results are given in Table-II.

**TABLE-II**

**HYDROGEN PEROXIDE BLEACHING OF CMP UNBLEACHED PULP FILTRATE**

Unbleached pulp consistency %	:	14.0
Unbleached pulp Filtrate colour pt-co units	:	6250
Unbleached pulp filtrate pH:		8.2

Sl. No.	Particulars	Unit	Results					
1.	Peroxide added	%	0.05	0.075	0.10	0.125	0.15	0.175
2.	Caustic Soda, NaOH	%	0.04	0.04	0.04	0.04	0.04	0.04
3.	Sodium Silicate (38 <sup>0</sup> Be)	%	0.25	0.25	0.25	0.25	0.25	0.25
4.	Magnesium Sulphate	%	0.005	0.005	0.005	0.005	0.005	0.005
5.	Initial pH	-	10.2	10.2	10.2	10.2	10.2	10.2
6.	Final pH	-	9.7	9.7	9.7	9.7	9.7	9.7
7.	Residual Peroxide	%	0.024	0.025	0.027	0.028	0.029	0.034
8.	Residual colour pt-co units		2500	2000	1750	1500	1300	1100
<b>Constant Conditions</b>								
	Temperature °C	:	75					
	Reaction time min	:	120					

**RESULTS AND DISCUSSION**

**PEROXIDE BLEACHING OF UNBLEACHED CHEMIMECHANICAL PULP**

The unbleached chemimechanical pulp from mixed hard woods used for the study was having a brightness of 36.3%.

The bleaching results of Table-I can be summarised as follows:

Peroxide addition%	Brightness of bleached pulp%	
	At 10% cy	At 20% cy
3.0	60.2	63.3
3.5	-	64.8
4.0	61.7	66.5
4.5	-	67.5
5.0	64.1	68.3
5.5	-	68.9

6.0	65.6	-
6.5	-	-
7.0	66.4	-

From the above results as well as from **Figure-2** it can be seen that to attain 65.0% brightness for the bleached pulp the hydrogen peroxide requirement is 5.5% at 10% consistency and 3.5% at 20% consistency. This shows that by increasing the consistency to 20% from 10%, the peroxide requirement comes down by 2.0% (20 Kg/MT) which is equivalent to 36.4% in absolute terms. The residual peroxide at 10% consistency remained with pulp after bleaching varied between 26.0% to 28.5% of the peroxide addition. At 20% consistency also, the residual peroxide is almost in the same range which varied between 24.0% to 26.2% of the peroxide addition. The residual peroxide has become inactive mainly due to drop in pH. This residual peroxide can be reused by recirculating it in the process at higher pH conditions.

The curves in **Figure-2** indicated that on actual peroxide consumed basis, at 20% consistency, there is an improvement of 4-5 brightness units over 10%

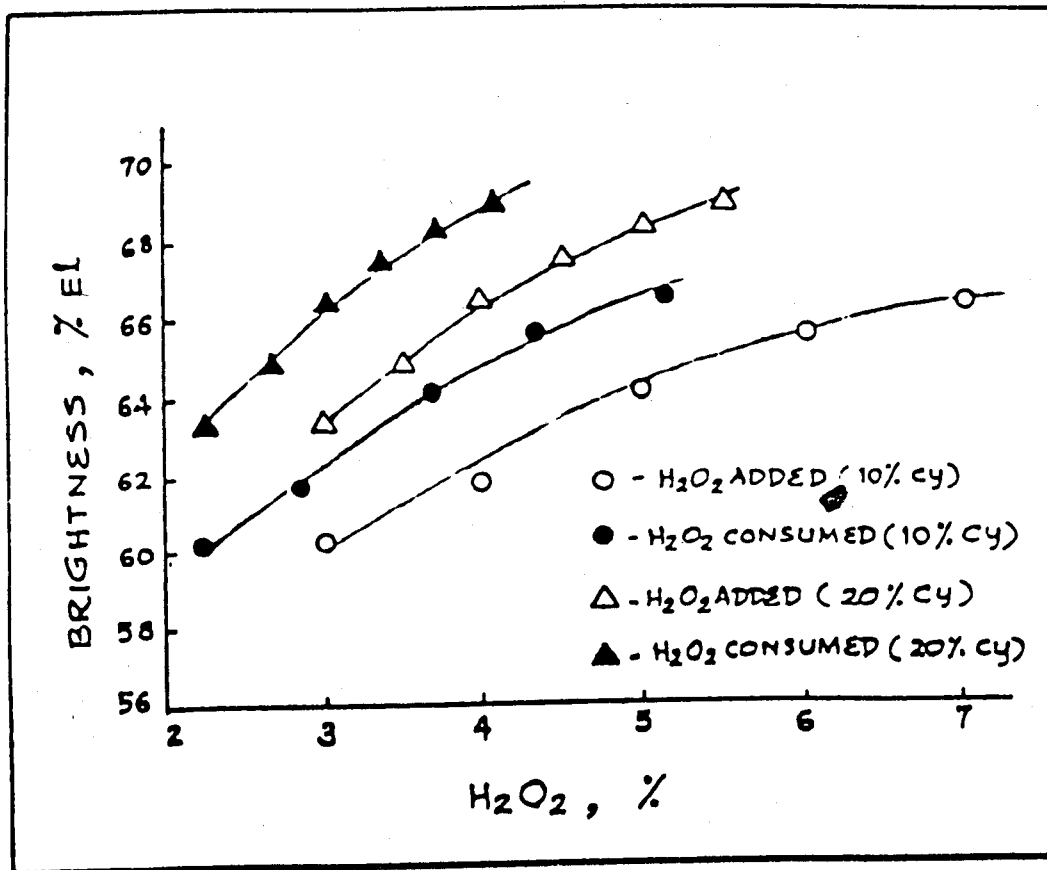


Fig.2. Hydrogen Peroxide Bleaching Of Hardwood Chemi Mechanical Pulp.

consistency, at 3.0 to 4.0% peroxide addition. The actual peroxide consumed for 65% pulp brightness is 4.10% at 10% consistency and 2.65% at 20% consistency. This clearly shows that there is a considerable reduction in peroxide consumption to the extent of 1.45% (14.5 kg/MT) by increasing the consistency from 10% to 20% during bleaching. The reduction in peroxide on addition and consumption basis are almost identical which is 36.4 and 35.4% respectively when the bleaching consistency is increased from 10% to 20% for a target brightness of 65% for the bleached pulp.

#### PEROXIDE BLEACHING OF UNBLEACHED PULP FILTRATE

The bleached pulp filtrate colour from chemimechanical pulp mill is about 1100 pt-co units.

The results from Table-II indicate that for leaching of unbleached pulp filtrate, having a colour of 6250 pt-co units to a residual colour of 1100 pt-co units, the peroxide requirement is 0.175% on the filtrate basis. The consumption pattern of H<sub>2</sub>O<sub>2</sub> in the bleaching of unbleached chemimechanical pulp, as given in Table-III and Fig.4 show that, in terms of equivalent peroxide on pulp, the H<sub>2</sub>O<sub>2</sub> requirement for bleaching unbleached pulp filtrate alone is 1.57% at 10% consistency and 0.70% at 20% consistency, showing 55.4% reduction in absolute terms when the consistency is increased from 10% to 20%. The reduction of peroxide consumption for unbleach pulp filtrate at 20% consistency bleaching in comparison to 10% consistency bleaching is due to reduced volume of coloured unbleach filtrate remaining with the pulp at 20% consistency. It is

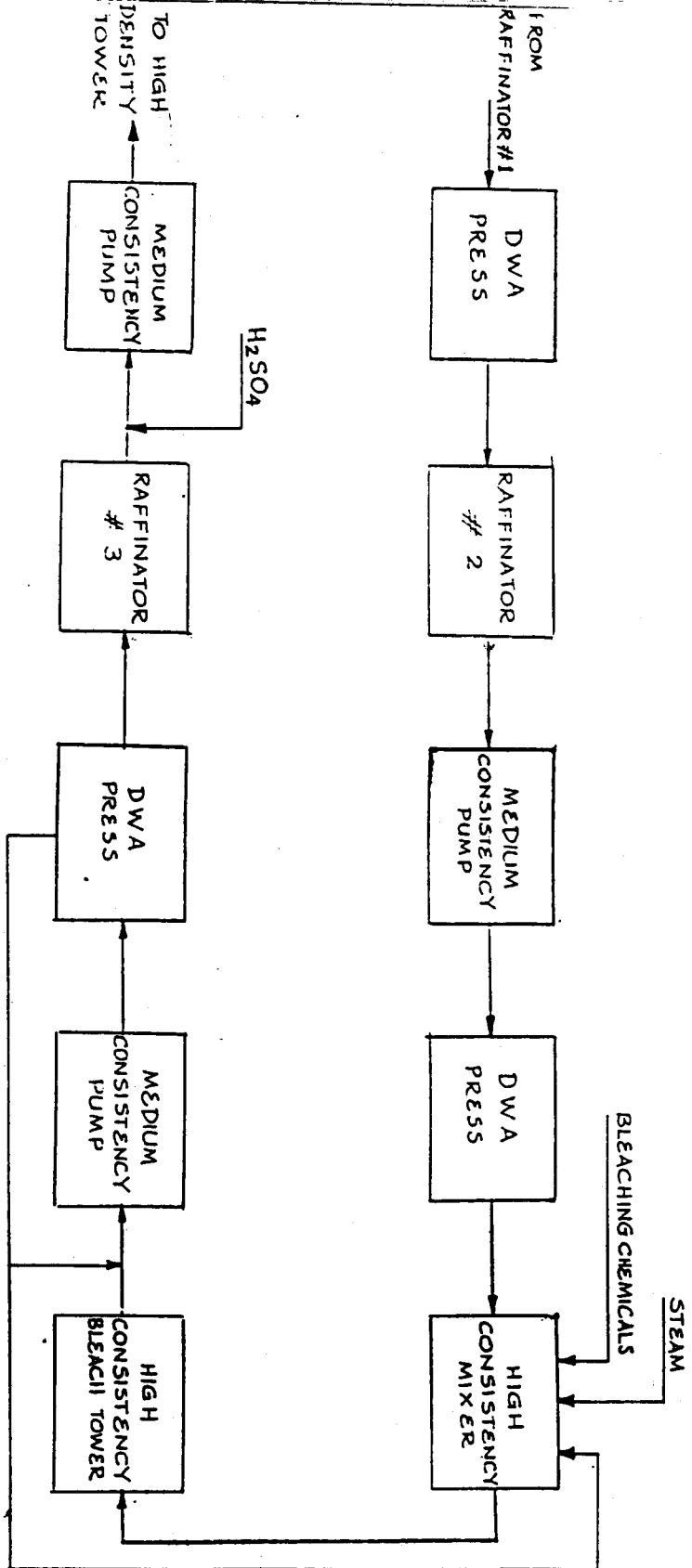


Fig.3. Block Diagram Of Proposed High Consistency Hydrogen Peroxide Bleaching System Of Chemimechanical Pulp At HNL



TABLE-III					
CONSUMPTION PATTERN OF HYDROGEN PEROXIDE IN THE BLEACHING OF UNBLEACHED CHEMI-MECHANICAL PULP					
Sl. No.	Particulars	UNITS	RESULTS		REDUCTION
	Consistency	%	10	20	-
1.	Unbleached pulp Brightness	%	36.3	36.3	-
2.	Hydrogen Peroxide (100%) requirement for bleaching	%	5.5	3.5	2.0
3.	Residual Peroxide (100%)	%	1.40	0.85	0.55
4.	Hydrogen Peroxide (100%) consumed for bleaching	%	4.10	2.65	1.45
5.	H <sub>2</sub> O <sub>2</sub> (100%) requirement for bleaching of unbleach pulp filtrate (equivalent peroxide on pulp)	%	1.57	0.70	0.87
6.	H <sub>2</sub> O <sub>2</sub> (100%) requirement for bleaching of pulp by difference. Sl. No. 2-3)	%	2.53	1.95	0.58
7.	H <sub>2</sub> O <sub>2</sub> (100%) consumed by pulp alone for bleaching on the actual consumption	%	61.7	73.5	-
8.	Bleached pulp Brightness	%	65.0	65.0	-

to be understood that the amount of unbleached filtrate is reduced by 55.6% when the pulp consistency is increased from 10% to 20%. The reduction in hydrogen peroxide consumption (55.4%) for the bleaching of the coloured filtrate is in close agreement with the reduction in its volume (55.6%) when the consistency is increased from 10% to 20%. The Hydrogen Peroxide (100%) required for bleaching pulp alone is 2.53% at 10% consistency and 1.95% at 20% consistency showing 22.9% reduction (in absolute terms) in peroxide consumption with increased consistency for a target brightness of 65% for the bleached pulp. However in the actual bleaching of the pulp the peroxide consumption has reduced by 1.45% (14.5 kg/MT) with increased consistency to achieve 65% brightness for the bleached pulp. Out of this 14.5 kg/MT reduction, 8.7 kg/MT reduction (60%) is on account of reduction in the unbleach filtrate volume at 20% consistency and 5.8 kg/MT reduction (40%) is on account of higher peroxide concentration during bleaching due to high consistency.

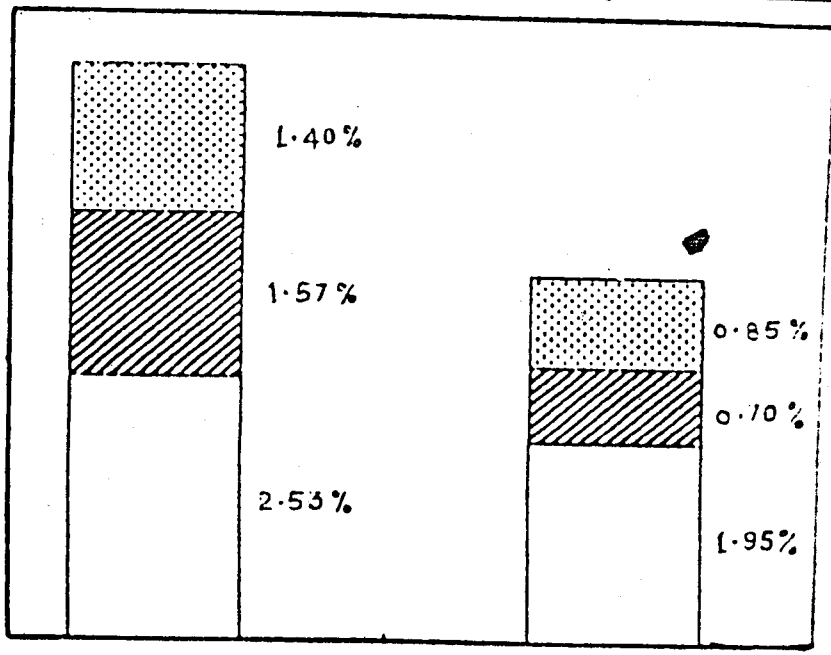
Out of the total peroxide consumed at 10% and 20% consistency, the proportion of peroxide

consumed by pulp at 20% consistency is higher i.e. 73.5% in comparison to the peroxide consumed by the pulp at 10% consistency i.e. 61.7%. This clearly shows that out of the quantity of peroxide consumed, a higher proportion of peroxide is reacting with the pulp at 20% consistency in comparison to 10% consistency during peroxide bleaching, which helps in gaining higher brightness at lower hydrogen peroxide addition.

#### OBSERVATIONS

1. High brightness hard wood chemimechanical pulp for using in newsprint furnish can be produced with high consistency hydrogen peroxide bleaching at a moderate peroxide addition.
2. H<sub>2</sub>O<sub>2</sub> requirement in the bleaching of hard wood chemimechanical pulp reduces by 36.4% for a target brightness of 65%, when the consistency is increased from 10% to 20% during bleaching. In terms of quantity the peroxide requirement reduces by 20 kg/MT.

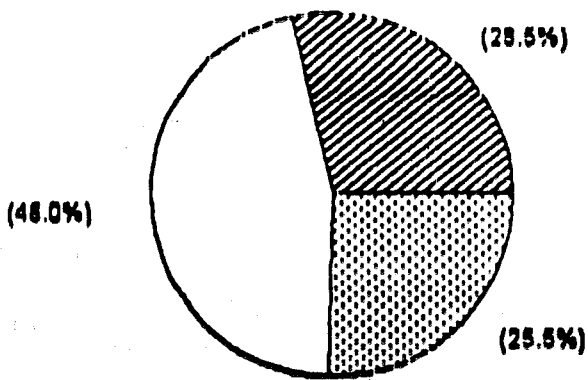
□ PULP  
 ▨ UNBLEACH FILTRATE  
 ▩ RESIDUAL PEROXIDE



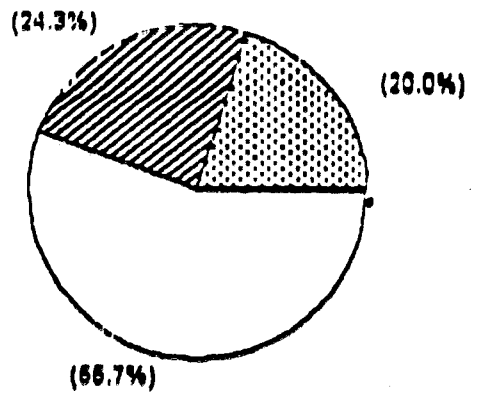
5.5% ←-- PEROXIDE CHARGE --> 3.5%

10% CONSISTENCY

20% CONSISTENCY



10% CONSISTENCY



20% CONSISTENCY

3. On the basis of actual consumption, the peroxide consumption reduces by 35.4% (from a peroxide consumption of 4.10% at 10% consistency to 2.65% at 20% consistency) when the consistency is increased from 10% to 20%. In terms of quantity, peroxide consumption reduces by 14.5 kg/MT.
4. There is a reduction of 14.5 kg/MT peroxide due to high consistency bleaching, on the actual consumption basis. Out of this, 60.0% reduction is due to reduction in unbleach pulp filtrate at high consistency and the balance 40.0% is due to high concentration of peroxide during reaction.

Based on the above encouraging results with high consistency hydrogen peroxide bleaching, to improve the brightness of chemimechanical pulp for using in newsprint furnish to produce newsprint of higher brightness (60-62%), HNL is embarking to high consistency hydrogen peroxide bleaching of chemimechanical pulp replacing the medium consistency peroxide bleaching. The proposed high consistency peroxide bleaching system is shown in **Figure-3**.

#### **PROPOSED HIGH-CONSISTENCY PEROXIDE BLEACHING SYSTEM**

The unbleached pulp from Raffinator-2 is pumped to DWA Press through a M.C. Pump. The unbleached pulp is dewatered to 30-35% consistency in DWA press from where the pulp enter a high consistency mixer and then fall into a downward flow bleach tower. Bleach chemicals (hydrogen peroxide, soup solution and magnesium sulphate) are added to the pulp before entering to high consistency mixer. LP steam is given at the mixer. The consistency in the bleach tower is maintained at 20-25%. A retention time of 2 hours is given at 75°C temperature. The bleached pulp after ring dilution is pumped to another DWA Press. The bleach filtrate from DWA Press is used for ring dilution at the bottom of the bleach tower as well as for adjusting the consistency at HC mixer.

The bleached pulp from DWA press is refined in the Raffinator-3 at high consistency. The refined pulp from Raffinator-3 is pumped to HD tower

through an MC Pump after acidifying the pulp to 5.5 pH with sulphuric acid.

In addition to the improvement in the brightness of pulp, at high consistency peroxide bleaching, the peroxide dose can be reduced further in the plant scale due to the recycling of residual peroxide in the bleach filtrate at the bleach tower feed point. By adopting the high consistency bleaching system HNL is confident of achieving the high brightness (65%) for the bleached chemimechanical pulp with the similar amount of hydrogen peroxide being consumed presently. The introduction of DWA press in dewatering the bleached pulp not only helps in utilising the residual peroxide in filtrate but also helps in refining the bleached pulp at higher consistency of 30% in Raffinator-3 which is likely to improve the pulp properties due to high consistency refining.

#### **ACKNOWLEDGEMENT**

The authors are grateful to the management of Hindustan Newsprint Ltd. for allowing them to publish this paper.

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