Hydrogen peroxide bleaching for newsprint grade chemical pulp

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SUMMARY

Use of chlorine as a bleaching chemical for pulp bleaching produces toxic chlorinated organic compounds. Due to this, in the developed countries, chlorine is replaced by other bleaching agents like Oxygen, Hydrogen Peroxide, Chlorine dioxide, Ozone and Enzyme. India has to work in this direction.

At Hindustan Newsprint Limited as a first phase, the calcium hypochlorite bleaching of chemimechanical pulp is replaced by hydrogen peroxide bleaching. In the second phase, laboratory studies have established that, the calcium hypochlorite stage of the CH bleaching of chemical pulp can be replaced by hydrogen peroxide, making the bleaching sequence as CP.

Adopting a peroxide stage after the initial chlorination stage, gives a better pulp with respect to viscosity, strength and optical properties HNL is organising a plant scale trial to establish the techno economic benefits.

Introduction

Chlorine has remained as the principal bleaching agent in Indian Pulp and Pader Industry. Though chlorine dioxide and Hydrogen Peroxide are being used in some cases of bleaching of pulp for speciality grade paper and in some cases oxygen bleaching has been introduced, the conventional CEH or CEHH bleaching sequence are generally followed in the Indian Pulp and Paper Industry. In developed countries chlorine is being slowly eliminated from the bleaching sequences and trend is for switching over to oxygen, hydrogen peroxide, ozone and enzyeme bleaching, because the toxic chlorinated organic compounds (AOX) generated during the chlorine bleaching have adverse effect on the environment. However, in the Indian contet, this awareness has not yet come up. None-the-less the Indian Pulp and Paper Industry should put in all efforts to find out alternate bleaching agents, before it is enforced. Hindustan Newsprint Ltd. is working in this direction.

At Hindustan Newsprint Ltd, the 220 TPD chemimechanical pulp mill was designed for calcium hypochlorite bleaching and the 100 TPD chemical pulp mill for CEH bleaching. The high priority for a cleaner environment at HNL successfully suspended the extraction stage in the chemical pulp bleaching due to the very high colour discharged from this stage thus making the bleaching sequence as CH. Calcium hypochlorite was used in two stages for the bleaching of Eucalyptus chemimechanical pulp upto 1989. From 1990, HNL has switched over to Hydrogen peroxide bleaching of its chemimechanical pulp, completely eliminating the use of chlorine in this section. Now HNL has put up a full fledged system for the transportation, storage and handling of hydrogen peroxide for the bleaching of chemimechanical pulp. The advantage of hydrogen peroxide lies in its ease of handling and appli-

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cation, its versatility and the relatively non-toxic and innocuous nature of its reaction products.

Eventhough the use of hydrogen peroxide for the bleaching of both chemical pulps is well known, It is not being used in the Indian Pulp and Paper mills primarily due to its very high cost. However, HNL has experienced that, only the bleaching cost should not be considered in the application of hydrogen peroxide. It is established that if we consider the overall benefits, the constlior bleaching chemicals like hydrogen peroxide may prove economical in replacing chlorine in bleaching.

Fascinated by the results of hydrogen peroxide bleaching in chemimechanical pulp mill, HNL took up a study on the bleaching of chemical pulp using hydrogen peroxide.

After studying a number of permutations and combinations it was found that adopting a single stage peroxide after the chlorination stage, making the bleaching sequence as CP, could be the most beneficial bleaching sequence for chemical pulp.

Results and Discussion

The study reported is on the bleaching of reed (Ochlandra Travan Cori) kraft pulp which is the major rawmaterial for the chemical pulp at HNL. Unbleached pulp of different kappa number varying between 15 to 30 are prepared in the laboratory and bleached seperately using the CP sequence and the conventional CH sequence to a brightness of about 65%. The bleaching chemicals requirement to achieve this brightness is given in Table I. Table II gives the bleached pulp yield, viscosity and the ash of the bleached pulp. The

TABLE—I

BLEACHING CHEMICALS REQUIRED FOR PULPS OF DIFFERENT KAPPA NUMBERS

Unbleached pulp kappa number			29.0	25.0	20.3	15.6
Bleaching Sequence	Bleaching Chemicals	Unit				
CH	Chlorine	%	5.25	4.9	4.0	3.15
	Hypo	%	3.2	3.0	2.4	2.1
	Brightness	%	66.3	67.0	64.4	69.0
CP	Chlorine	%	5.25	4.9	4.0	3.15
	Peroxide	%	1.5	1.5	1.2	1.0
	Brightness	%	65.6	66.5	64.0	64.1

TABLE—II

YIELD, VISCOSITY AND ASH OF THE PULPS

Unbleached pulp kappa number			29.0	25.0	20.3	15.6
Bleaching Sequence	Parameter	Unit				
Unbleached Pulp	Yield	%	57.5	57.0	55 8	55.0
	Viscosity	cp	53.8	45.5	43 6	34.0
	Ash	%	1.20	1.24	1.27	1.27
CH	Yield	%	54.1	53.2	52.9	52.6
	Viscosity	cp	26.9	26 9	27 9	21.8
	Ash	%	0 77	0.87	0 81	0.97
CP	Yield	%	54.5	53.7	53.3	53.1
	Viscosity	cp	33.0	32.8	34.2	26.2
	Ash	%	0.48	0.50	0.47	0 39

optical properties of the various bleached pulps are recorded in Table III. The initial freeness of the bleached pulp, their beating time to get 300 ml CSF in the laboratory Hollander beater and the wet web strength of the pulps at 300 ml CSF are given in Table IV. The strength properties of the pupls with respect to breaking length, tear factor and burst factor at 300 ml CSF and the porosity are given in Table V.

Bleaching Chemical Requirement

The results given in Table I show that for unbleached pulp of kappa Number of 29, the total chlorine requirement is 8.45% with 5.25% in chlorination stage and 3 2% in the hypo stage to get 66.3% brightness using the CH sequence. In case of CP sequence the peroxide requirement is 1·5% to achieve similar brightness which means that 3.2% hypo can be replaced by 1.5% hydrogen peroxide, maintaining the same chlorine (5.25%) in the initial chlorination stage.

For 25 kappa number reed unbleached pulp, the total chlorine requirement is 7.9% in CH sequence with 4 9% in chlorination and 3% in hypo stage. In CP sequence maintaining the same chlorine (4.9%) in the chlorination stage, the 3% chlorine used in the hypo stage can be replaced by 1.5% hydrogen peroxide. In case of unbleached pulp of kappa number 20 3 the total chlorine requirement in CH sequence is 6.4% with 4% in chlorination stage and 2.4% in hypo stage. When we used hydrogen peroxide as in CP seq-

TABLE—III

OPTICAL PROPERTIES OF THE PULPS

Unbleached Pulp kappa number			29.0	25.0	20.3	15.6
Bleaching Sequence	Parameter	Unit				
Unbleached pulp	Brightness	%	29.3	31.4	33.4	34.9
CH	Brightness	%	66 3	67.0	64 4	69.0
	Yellowness	%	22 5	21.2	22.7	18.0
	Opacity	%	77.6	76.2	77.4	76 6
	PC Number		8 6	8.3	7.9	9.3
CP	Brightness	%	65.6	66.5	64.0	64.1
	Yellowness	%	21.2	20.6	22.2	20.5
	Opacity	%	78 4	76.3	79.9	80.9
	PC Number		4.2	3.6	4 5	3.7

TABLE—IV

INITIAL FREENESS, BEATING TIME AND WET WEB STRENGTH OF THE PULPS

Unbleached pulp Kappa Number			29.0	25.0	20.3	15 6
Bleaching sequence	Parameter	Unit				
CH	Freeness	ml CSF	695	680	690	700
	Beating time	min	26 0	27.0	28.0	25.5
	Wet Web strength	Nm/g	3.03	3.04	2.90	2.86
CP	Freeness	ml CSF	700	710	710	710
	Beating time	min	24.5	28.0	28.5	29.0
	Wet web strength	Nm/g	3.03	3.47	3.33	3.62

Note : 1. Beating time is for attajning 300 ml CSF in Laboratory Hollandor beater.
2. The wet web strength reported is at 300 ml CSF.

TABLE–V

PHYSICAL STRENGTH PROPERTIES OF THE BLEACHED PULPS AT 300 ML CSF

Unbleached pulp kappa number			29.0	25.0	20.3	15.6
Bleaching sequence	Parameters	Unit				
CH	Tensile Index	Nm/g	66.56	67.57	70.9	71.3
	Tear Index	mNm^2/g	10.77	10.51	9.83	10.17
	Burst Index	$KPam^2/g$	4.78	5.14	4.86	5.04
	Porosity	ml/min	124	77	83	77
CP	Tensile Index	Nm/g	67.28	68.93	73.31	74 28
	Tear Index	mNm^2/g	11.47	10. 6	11.59	10 09
	Burst Index	$KPam^2/g$	5.33	4.81	5.20	5.02
	Porosity	ml/min	140	104	110	104

uence, the 2.4% hypo can be replaced by .2% hydrogen peroxide.

When the unbleached pulp kappa number is 15 6 the total chlorine requirement in CH sequence is5 25% with 3.15% in chlorination stage and 2.1% in hypo stage With CP sequence the 2.1% hypo in second stage can be replaced by 1.0% of hydrogen peroxide.

The above results show that the chlorine requirement for different kappa number unbleaced pulp; bleached by CH sequence gradually decreases with decreasing kappa number. The total chlorine requirement is 8.45% for 29.0 kappa number, 7.9% for 25.0 kappa number, 6.4% for 20.3 kappa number and 5.25% for 15.6 kappa number unbleached pulp.

With CP sequence the peroxide requirement is 1.5% for both 29.0 kappa number and 25.0 kappa number pulps. It is 1.2% for 20 3 kappa number pulp and 1.0% for 15.6 kappa number pulp with normal chlorine in the chlorination stage as used in the conventional CH sequence. These results indicate that the peroxide requirement decreases from 1.5% to 1.0% when the kappa number is reduced from 29-25 to 15 6.

Pulp Yield

The pulp yield results given in Table II shows that there is a drop of unbleached pulp yield by 2.5% from 57.5% to 55% when the unbleached pulp kappa number is reduced from 29.0 to 15.6. The extent of this drop in yield is reduced to 1.5% for the bleached pulp from CH sequence and 1.4% with CP sequence. The yield loss in bleaching decreases as the original unbleached pulp kappa number decreases. There is a marginal advantage of increase in yield by 0.4–0 5% with the CP sequence over CH sequence, at any level of kappa number of unbleached pulp.

Viscosity

The reed unbleached pulp has CED viscosity of 53 8 cps, 45.5 cps, 43 6 cps and 34 0 cps at 29 0, 25.0, 20.3 and 15.6 kappa number, showing that there is a gradual drop in the viscosity of unbleached pulp as its kappa number decreases. However, the drop in viscosity in bleaching is more when the kappa number of the starting unbleached pulp is high With the CH sequence the drop is 50%, with 29.0 kappa number pulp and 40.8% with 25 0 kappa number pulp. Then the drop remains almost 36% for 20 3 and 15.6 kappa number pulps. With CP sequence the drop in viscosity in bleaching is 38.7% with 29.0 kappa number pulp and 27.9% with 25.0 kappa number pulp. Thereafter the drop remains alomst 22% for the unbleached pulp of kappa number 20 3 and 15.6. This shows that by replacing the hypochlorite stage with hydrogen peroxide, a gain of 22% in the viscosity of the bleached pulp is achieved. This means a gain of about 5–6 units in viscosity depending upon the kappa number of the unbleached pulp by adopting hydrogen peroxide stage of bleaching. Another observation from the results of bleached pulp viscosity is that there is no appreciable drop in the bleached pulp viscosity when

the kappa number of the original unbleached pulp is reduced from 29.0 to 20.3 and bleached using a particular bleaching sequence to 65-66% brightness. However, a sudden drop in bleached pulp viscosity is observed when the kappa number of the original unbleached pulp is reduced from 20 3 to 15.6

This indicates that to get the best viscosity for the bleached pulp the kappa number of the unbleached pulp should be around 20 and a peroxide stage after the initial chlorination stage. Keeping the unbleached pulp kappa number around 20 also brings down the peroxide requirement to 1.2%.

Ash Content

The ash content in the reed unbleached pulp is in the range of 1.20 to 1.27% in the kappa number range of 29.0 to 15.6.

The ash centent in the bleached pulp obtained using CH bleaching sequence varied from 0.77 to 0.97% over the variation of original unbleached pulp kappa number from 29 0 to 15.6. For the bleached pulp using CP sequence, the ash content varied from 0.39 to 0.50%. These figures clearly indicate that the ash content in the bleached pulp is reduced by nearly 40% by replacing the calcium hypochlorite by hydrogen peroxide in the second stage. This reduction in ash is due to the elimination of troublesome calcium compounds carried along with the pulp.

Brightness :

As can be seen from the results in Table III, brightness of the unbleached pulp is 29.3% at 29 0 kappa number which gradually increases to 34.9% for 15.6 kappa number. The increase in brightness of unbleached pulp is almost linear upto a kappa number of 20. A 4% increase in brightness is obtained when the kappa number is reduced from 29.0 to 20 3, which is responsible for a proportionate reduction in the bleaching chemicals, The total chlorine requirement is reduced by 2.05% which consist of 1.25% as elemental chlorine and 0 8% as hypochlorite in the CH sequence when the kappa number of unbleached pulp is reduced from 29 to 20.3. In case of CP sequence the reduction in bleaching chemicals is 1 25% as elemental chlorine and 0.3% as hydrogen peroxide. The brightness values of the bleached pulps given in Table III show that it is possible to achieve the desired brightness by adopting the CP sequence.

Yellowness :

The results of yellowness for the various bleached pulp given in Table III show that eventhough the brightness of the pulp from CP sequence are marginally lower than the corresponding pulp from CH sequence, the yellowness of the pulps from CP sequence are lower than that from CH sequence. This clearly indicates that the yellowness of the peroxide bleached chemical pulp is definitely lower than hypo chlorite bleached pulp. It is expected that the decrease in yellowness will be about 2% when compared at the same brightness level. This is an important factor for the newsprint pulp furnishes.

Opacity :

The opacity values of the various bleached pulps at 300 ml CSF as given in Table III are 77.6, 76 2, 77.4 and 76.6% respectively for the pulp obtained from the original unbleached pulp of kappa number 29.0, 25.0, 20.3 and 15.6 and bleached by CH sequence. However, when the hypochlorite was replaced by hydrogen peroxide as in CP sequence the corresponding opacity values are 78.4, 76.3, 79.9 and 80.9% respectively. These opacity values for the peroxide bleached pulp bring out a clear increase in the opacity over the hypochlorite bleached pulp. The increase is higher when the kappa number of the original pulp is low in the range of 20 3 to 15.6.

Post Colour (PC) Number :

The PC number for the pulps bleached by CH sequence varies from 7.9 to 9.3 for the variation of the kappa number from 29.0 to 15.6 of the starting unbleached pulp. The same pulps when bleached using the CP sequence the PC number of the bleached pulp varied from 3.6 to 4.5. These results indicate that adopting hydrogen peroxide as the second stage in two stage bleaching as CP sequence instead of the conventional hypochlorite i.e. CH sequence, the PC number of the bleached pulp can be reduced by about 50% which means that the brightness reversion for the bleached pulp can be significantly reduced or in otherwords the brightness stability is improved by adopting the peroxide stage in place of the hypochlorite stage

which could mean that there is a possibility of reducing the targeted brightness by a few points.

Freeness and Beating time :

The initial freeness of CH bleached pulp varied between 680–700 ml CSF for the pulps obtained from the different kappa number unbleached pulps. In case of the pulp bleached using CP sequence the freeness varied from 700–710 ml CSF indicating that there is a marginal increase in the freeness of the CP bleached pulp. This has resulted in a marginaly increased beating time for the CP bleached pulps compared to CH bleached pulp.

Wet Web Strength :

The wet web strength of the CH bleached pulps at 300 ml CSF is 3.03, 3.04, 2.90 and 2 86 Nm/g respectively for the pulps obtained from the unbleached pulp of kappa number 29.0, 25.0, 20.3 and 15.6. A decreasing trend is noticed in the wet web strength with the decrease in the kappa number of the starting unbleached pulp. When the same pulps are bleached using hydrogen peroxide in the second stage as in CP sequence, the wet web strength varies from 3.03 to 3.62 Nm/g showing a slightly increasing trend with the decreasing kappa number of the starting unbleached pulp. These results clearly indicate that replacing calcium hypochlorite by hydrogen peroxide in the second stage will improve the wet web strength of the resultant chemical pulp which is very much desirable in the machine runnability with the already weak newsprint stock.

Tensile Index :

The tensile index at 300 ml CSF for the pulps bleached using CH sequence are 66,56, 67.57, 70.9 and 71.3 Nm/g respectively for the pulps obtained from the original unbleached pulp of kappa number 29.0, 25.0, 20.3 and 15.6. When peroxide was used in the second stage replacing the hypochlorite, the corresponding tensile index values are 67.28, 68.93, 73.31 and 74 28 Nm/g. An increasing trend in the tensile index is observed with the decreasing kappa number of the starting unbleached pulp both in case of CH and CP bleached pulp. Again the tensile index for the CP bleached pulps are generally higher than that for CH bleached pulps in the kappa number range studied.

Tear Index :

The tear index at 300 ml CSF for the bleached pulp obtained from CH sequence are 10.77, 10.51, 9.83 and 10.17 mNm^2/g for the pulps obtained from the original unbleached pulp of kappa number 29.0, 25.0,20.3 and 15.6 respectively. This tear index remains more or less uniform over the variation in the kappa number of the unbleached pulp. The corresponding tear index values for the CP bleached pulps are 11 47, 10 06, 11.59 and 10 9 mNm^2/g. From these results it may be observed that generally the tear index of the CP bleached pulps are higher than for CH bleached pulps.

Burst Index :

The burst index values at 300 ml CSF for the CH bleached pulps are 4.78, 5.14, 4.86 and 5 04 k Pam^2/g respectively for the pulps obtained from the starting unbleached pulp of kappa number 29 0, 25.0, 20.3 and 15.6. The corresponding tear index values for the CP bleached pulps are 5.33, 4 81, 5.20 and 5.02 k Pam^2/g respectively. Here also we may see that except for slight deviation generally the burst index for the CP bleached pulps are higher than for CH bleached pulps.

Porosity :

The Bendtsen porosity of the bleached pulps from CH sequence at 300 ml CSF are 124, 77, 83 and 77 ml/min respectively for the pulps obtained from the unbleached pulp of kappa number 29.0, 25.0, 20.3 and 15.6. The corresponding porosity values for the CP bleached pulps are 140, 104, 110 and 104 ml/min respectively. These results show that the porosity of the CP bleached pulps are generally higher than for CH bleached pulps. This perhaps may be due to the fact that the CP bleached pulps contain less ash and fines compared to CH bleached pulps.

Conclusions :

1. Hydrogen peroxide can be used in the second stage in two stage bleaching sequence for producing semi bleached newsprint grade chemical pulp. The calcium hypochlorite can be replaced by hydrogen peroxide making the bleaching sequence as CP.

2. To keep the hydrogen peroxide consumption minimum and to get the best results for the bleached pulp, the kappa number of the unbleached pulp is to be maintained around 20.

3. For an unbleached pulp of kappa number 20, the hydrogen peroxide required is 1.2% (on 100% basis) after the initial chlorination using 4.0% chlorine. This will replace about 2.4% calcium hypochlorite (as available chlorine) to achieve a brightness of 64-65% for the bleached pulp.

4. A marginal advantage of increase in bleached pulp yield by 0.4 to 0.5% is possible by adopting hydrogen peroxide replacing calcium hypochlorite.

5. There is an improvement in the bleached pulp viscosity by about 22%, increasing it by about 5-6 cps when hydrogen peroxide is used in the second stage.

6. The ash content in the bleached pulp is reduced by nearly 40% by replacing calcium hypochlorite by hydrogen peroxide in the second stage.

7. The PC (Post Colour) number of the bleached pulp is reduced by about 50% by using hydrogen peroxide thereby increasing the brightness stability of the pulp.

8. The strength and optical properties of the pulp bleached with hydrogen peroxide in the second stage are better than calcium hypochlorite pulp.

Hindustan Newsprint Limited is organising a plant scale trial for establishing the techno-economic benefits of the CP bleaching sequence. If proved successful, this will be another step forward (after the initial hydrogen peroxide bleaching of chemimechanical pulp) towards the elimination of chlorine from bleaching making the bleaching process environmentally friendly.

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