Studies on brightness stability of peroxide bleached rice straw pulp with special reference to CHP bleaching sequence

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INTRODUCTION

The increased demand for paper and paper products due to growing population and increased level of literacy and civilisation has created problem of shortage of raw material all over the world. This problem is more severe in developing countries due to ruthless deforestation for fuel and timber and also due to lack of systematic afforestation. Naturally nonwood fiberous raw materials such as rice straw, wheat straw, bagasse, jute fibres and other local grasses as well as secondary fibres have become the source of raw material for paper.

Most of the small and medium size paper mills in India are based on agro residue such as rice straw, wheat straw, and bagasse and some of them are also based on secondary fibres. Our technologists and chemical engineers have developed sufficient expertise on pulping, processing and converting agro residue pulp in to various grades of paper. Some literature have been published on the pulping and bleaching of agro residue in Indian context (1 to 4).

Literature has also been published on studies of properties of agro residue mainly on rice straw (1). Straw has lower cellulose content than wood but inspite of its low cellulose content, it has total carbohydrate fraction (holocellulose) approximately equal to that of wood. This is due to high hemicellulose and low lignin content compared to wood. A typical analysis of rice straw is given in Table—1.

The properties of rice straw pulp depend upon the type of straw and the conditions of cooking. Soda process gives about 35% yield of pulp from straw. Straw fibres are short, averaging 0.8 to 1.5mm in length but ratio of fibre length : fibre diameter is high (5). Due to its high hemicellulose content it has easy hydrating properties.

TABLE—1 : Typical Chemical Analysis of Rice Straw

Sr. No.	Particulars*	Results %
1.	Moisture	6.67
2.	Ash	15.0
3.	Cold water solubility	11.0
4.	Hot water solubility	13.5
5.	1.0% NaOH solubility	44.3
6.	Alcohol-Benzene solubility	5.9
7.	Holocellulose**	70.1
8.	Lignin	10.0

* Results are expressed on O.D. raw material basis
** Corrected for ash

BLEACHING OF RICE STRAW PULP

Rice straw pulp is very weak and therefore, requires to be refined and bleached preferably under mild conditions. In Indian context, some literature have published on bleaching of rice straw, wheat straw (1 to 4). In medium size paper mill, rice straw pulp is generally bleached by usage of C E H, sequence whereas in small paper mills, it is undertaken by CHH and H_1H_2 type of bleaching. Sometimes bleaching is carried out even by single stage hypo. This shows that agro residue pulp is generally bleached by usage

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of short bleaching sequences and not by multistage bleaching sequence as in case of wood or bamboo. These types of short bleaching sequences are advantageous from investment point of view, but agro residue being a raw material with short fibre length, degradation of fibres during bleaching by aggressive bleaching agent such as by hypochlorite should be avoided only. Similarly, a lot of literature is published on release of chlorinated organic compounds such as chloroform, dioxin etc. which are carcinogen in bleaching effluent of pulp mill by chlorine and chlorine based compounds. It is well reviewed by Hrutfiord and Negri(6). It is not possible to replace entire hypochlorite due to economic consideration. However, It is possible to reduce level of hypochlorite in CEH, CHH and in two stage hypochlorite bleaching by usage of non-toxic chemical viz., hydrogen peroxide (7 to 9).

A final bleaching stage with hydrogen peroxide is simple but elegant method of counteracting fluctuations in brightness. As the reaction conditions for peroxide bleaching are exceptionally flexible, this process can be conducted in a storage tower with good mixing facilities. The brightness increase is achieved all the more easily, when the initial brightness is lower. On the other hand, if the final brightness is high, the considerable increase in brightnesss can also be achieved by final bleaching with hydrogen peroxide (10). The important aspect of usage of hydrogen peroxide is the stability in final brightness of pulp. Colour reversion is particularly marked if hypochlorite is used at final stage of bleaching. Similarly, hypochlorite is non-specific bleaching agent while oxidising lignin, it also oxidises hemicellulose in the pulp. Due to this reason pulp becomes weak, and can not be bleached further. The strength to the paper can be imparted by blending the pulp with some long fibred pulp. However, brightness can not be improved further by use of any external agent. The efforts and money to make whiter pulp may be wasted if severe colour reversion is introduced by the method of bleaching. It is therefore, important to bleach the pulp to excellent brightness stability. In this paper, studies have been discussed with reference to rice straw pulp which is being bleached by CHH sequence in one of the pulp mills in India. The same bleaching sequence was modified to CHP at our Research Centre and studies on optical properties were carried out.

EXPERIMENTAL

The chlorinated rice straw pulp was collected from one of the leading small paper mills in Madhya Pradesh (M.P.). This chlorinated pulp was subjected for bleaching with different levels of Ca-hypochlorite. The hypochlorite bleached pulp after washing was further treated with different doses of hydrogen peroxide. The general parameters maintained during bleaching are given in Table-2. During hydrogen peroxide bleaching, the effect of various parameters like temperature, pH,the addition of caustic, sodium silicate etc. were studied. Wherever caustic and/or silicate were added, the initial pH was adjusted to 10.5. After peroxide bleaching the pulp was not washed, however, the sheets were made directly.

TABLE—2 : General Bleaching Parameters for Chlorinated Rice Straw Pulp

Parameters	Hypochlorite	Hydrogen Peroxide	
Consistency%	8	5	
Temperature °C	50	60	Ambient
Retention (min.)	60	60	60
pH : Initial	9.5-10.0	10·5	7.5
Final	7.5-8.0	8.0	7.0

TESTING

Brightness

The handsheets were dried in the air and their brightness values were measured on TECHNIBRITE Model TB-1C at effective wavelength of 457n.m which gives the brightness values directly in °ISO units.

Post Colour Number (P.C. Number)

The natural aging is very slow, and not reproducible, attempts have been made to speed up the aging process by exposure of pulp samples to higher temperature. The most common and simple aging test followed by most of the paper mills in India is heating in an oven at 105°C for 1 to 8 hours. In our studies, samples were kept in the oven at 105°C and they were withdrawn after every hour and this was continued up to 4 hours. The brightness values were measured aga-

in after aging and post colour number was calculated using the following equations :

1. $\frac{K}{S} \qquad \frac{(1-R)^2}{(2\ R)}$

2. P C No. $= 100 \times [(K/S)$ after ageing $-(K/S)$ before ageing$)]$.

Where K = Coefficient of absorption
S = Coefficient of scattering
R = Reflectivity $= \frac{\text{Brightness}}{100}$

The laboratory bleaching conditions and test results have been tabulated (Table 2 to 4), These results have been also discussed graphically (FIG. 1 to 9).

RESULTS AND DISCUSSION

1. It can be seen in FIG.—1 and Table—2 that brightness value of chlorinated rice straw pulp increases with increase in hypochlorite level. Here hypochlorite was used from 1% to 5% available chlorine level at first stage. However, as the level of hypochlorite increases, there is a tendency for 'brightness drop' after aging, also increases showing reversion in brightness of pulp (FIG. 2).

2. Brightness values of hypochlorite bleached rice straw pulp goes up even by use of very small level of hydrogen peroxide (0 1 to 0.2%) H_2O_2 (100%) on O.D. pulp. This is shown in FIG. 3. The increase in brightness value is quite rapid and may increase further with increase in hydrogen peroxide level when initial brightness is low. This may be due to formation of hypochlorous acid by reaction of residual hypochlorite and hydrogen peroxide added. This mixture of hypochlorous acid and hyderogen peroxide may be leading to active bleaching. However, all other cases show that the initial increase in brightness is very high, which does not improve further with increase in peroxide level. The brightness level obtained is more or less same with 0.1, 0.15 or 0.2% H_2O_2 (100%) on O.D. pulp.

3. Brightness values of rice straw pulp bleached by use of 2% hypochlorite and with various levels of hydrogen peroxide are shown graphically in FIG 4. The figure shows that the brightness values increase with increase in hydrogen peroxide level when bleached with proper buffer at elevated temperature. The temperature used during this experiment was 60°C.

4. The effect of temperature and buffer on brightness of rice straw pulp on aging is shown in

TABLE - 3 : EFFECT OF HYPOCHLORITE ON BRIGHTNESS OF RICE STRAW PULP

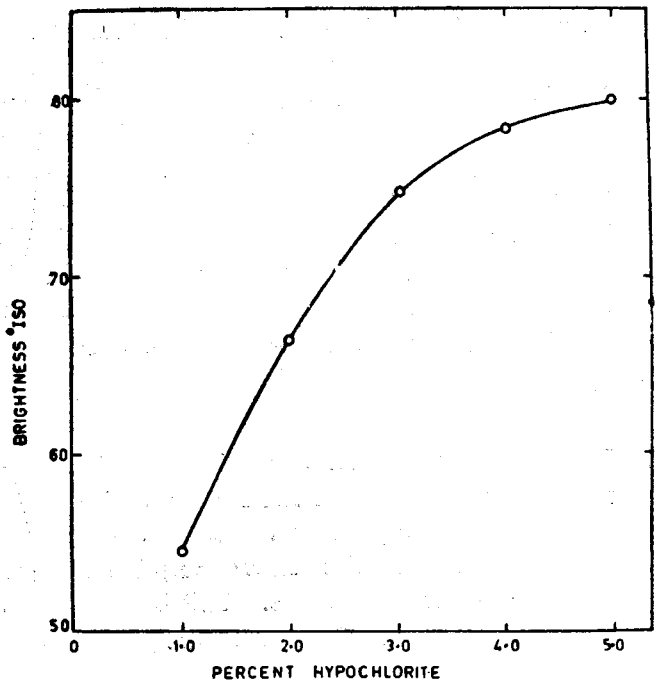
Parameters \ Sequence		1% HYPO				2% HYPO				3% HYPO				4% HYPO				5% HYPO			
1. Ca-Hypochlorite (A.C.) % on O.D. pulp		1.0	-	-	-	2.0	-	-	-	3.0	-	-	-	4.0	-	-	-	5.0	-	-	-
2. H_2O_2 (100%)	" "	-	0.1	0.15	0.2	-	0.1	0.15	0.2	-	0.1	0.15	0.2	-	0.1	0.15	0.2	-	0.1	0.15	0.2
3. NaOH	" "	0.5	-	-	-	0.5	-	-	-	0.5	-	-	-	0.5	-	-	-	0.5	-	-	-
4. Brightness °ISO		54.4	55.2	56.2	56.8	66.2	68.9	69.3	69.1	74.8	79.7	80.2	80.3	78.1	82.9	83.2	82.8	79.8	84.7	84.1	84.0
5. Brightness °ISO after heating in oven at 105°C :	1 hr.	53.5	54.4	55.4	55.6	64.3	66.8	67.1	66.9	71.1	75.0	75.3	75.1	73.8	77.7	78.1	77.6	75.3	78.9	77.9	77.4
	2 hr.	52.6	53.9	54.7	55.2	63.3	66.2	66.2	66.0	70.4	73.9	74.1	74.1	73.0	76.5	77.1	76.5	74.2	77.6	76.7	76.2
	3 hr.	52.3	53.7	54.5	54.9	62.9	65.4	65.6	65.5	69.7	73.3	73.6	73.6	72.5	76.1	76.6	76.5	73.7	76.9	76.0	75.5
	4 hr.	52.3	53.6	54.4	54.8	62.5	65.0	65.3	65.2	69.5	73.0	73.4	73.4	72.2	75.8	76.2	76.2	73.4	76.4	75.7	75.3
6. P.C. Number	1 hr.	1.1	0.9	1.2	1.3	1.3	1.2	1.3	1.3	1.6	1.6	1.6	1.7	1.6	1.4	1.4	1.4	1.5	1.4	1.6	1.8
	2 hr.	1.5	1.53	1.7	1.8	2.0	1.6	1.8	1.9	2.0	2.0	2.1	2.1	1.9	1.8	1.7	1.8	1.9	1.9	2.0	2.2
	3 hr.	1.7	1.8	1.9	2.1	2.3	2.1	2.2	2.2	2.3	2.3	2.3	2.3	2.1	2.0	1.9	2.0	2.1	2.1	2.3	2.5
	4 hr.	2.0	1.9	2.0	2.2	2.6	2.2	2.4	2.4	2.4	2.4	2.4	2.4	2.3	2.1	2.0	2.1	2.3	2.3	2.4	2.5

TABLE - 4 : EFFECT OF TEMPERATURE AND BUFFER ON BRIGHTNESS STABILITY OF RICE STRAW PULP BLEACHED WITH HYDROGEN PEROXIDE.

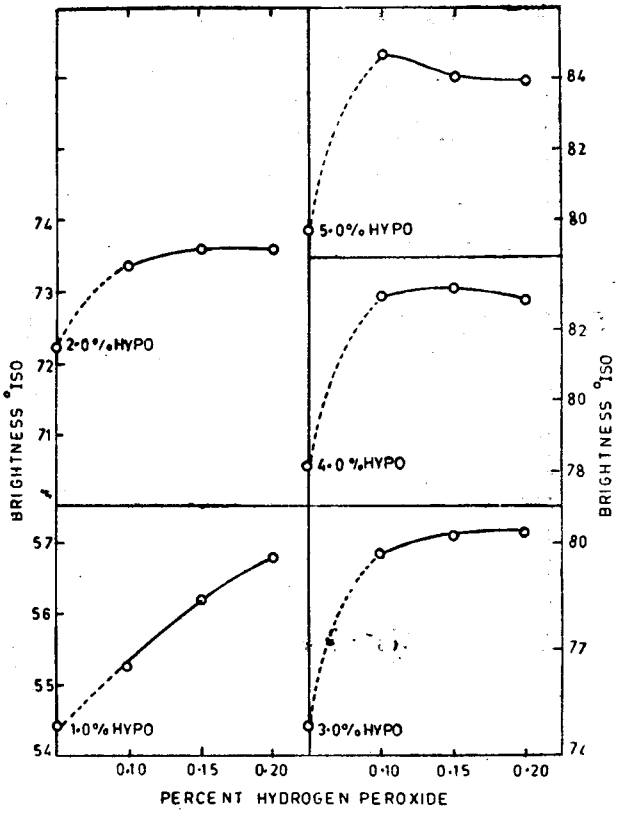
Parameters \ Sequence		Control	H_2O_2 at 60°C				H_2O_2 at Ambient Temp.			
1. Ca-Hypochlorite (A.C.) % on D.O. pulp		2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	
2. H_2O_2 (100%)	" "	-	0.1	0.15	0.2	0.2	0.2	0.2	0.2	
3. NaOH	" "	0.5	0.2	0.2	0.2	0.2	0.2	0.2	-	
4. Na-Silicate (38 °Be)	" "	-	0.1	0.1	0.1	-	0.1	-	-	
5. Brightness °ISO		71.8	72.5	73.3	74.4	74.8	74.5	73.8	72.9	
6. Brightness °ISO after heating at 105°C	: 1 hr.	68.8	70.6	71.0	72.4	72.0	71.4	71.0	69.9	
	2 hr.	67.9	69.5	70.1	71.1	71.0	70.2	70.2	69.0	
	3 hr.	67.4	69.0	69.6	70.7	70.6	70.0	69.7	68.4	
	4 hr.	66.9	68.7	69.1	70.1	70.2	69.6	69.5	68.0	
7. Post Colour Number	1 hr.	1.54	0.91	1.06	0.86	1.2	1.36	1.27	1.44	
	2 hr.	2.05	1.50	1.51	1.47	1.68	1.96	1.67	1.92	
	3.hr.	2.35	1.75	1.78	1.67	1.88	2.06	1.93	2.27	
	4 hr.	2.65	1.91	2.04	1.97	2.08	2.28	2.04	2.49	

TABLE - 5 : EFFECT OF TEMPERATURE AND BUFFER ON BRIGHTNESS STABILITY OF RICE STRAW PULP BLEACHED WITH HYDROGEN PEROXIDE.

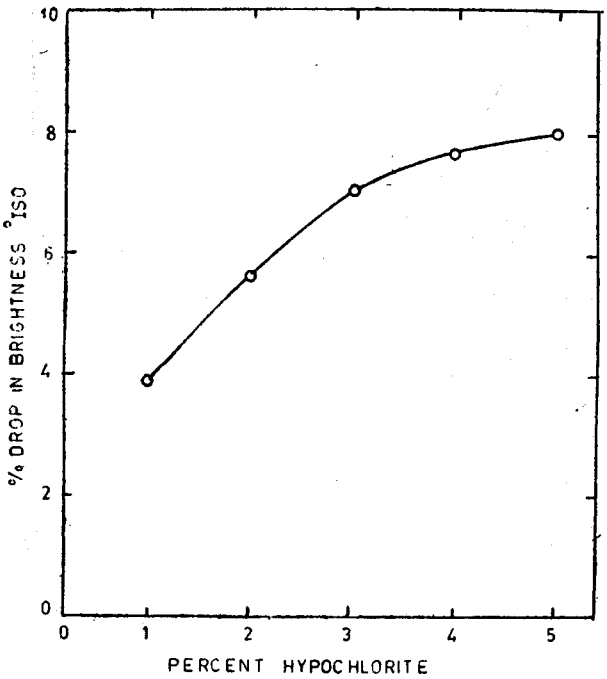
Parameters \ Sequence		Control	H_2O_2 at 60°C			H_2O_2 at Ambient	
1. Ca-Hypochlorite (A.C) % on O.D. pulp		3.0	3.0	3.0	3.0	3.0	3.0
2. H_2O_2(100%)	" "	-	0.1	0.15	0.2	0.1	0.1
3. NaOH %	" "	0.5	0.2	0.2	0.2	0.2	-
4. Na-Silicate (38°BC)	" "	-	0.1	0.1	0.1	0.1	-
5. Brightness °ISO		77.6	78.6	79.3	78.4	77.3	77.8
Brightness °ISO after heating at 105°C	: 1 hr.	72.9	75.5	75.8	74.9	73.3	73.3
	2 hr.	71.8	74.5	74.8	73.9	72.2	72.1
	3 hr.	71.1	73.9	74.0	73.5	71.5	71.5
	4 hr.	70.8	73.6	73.8	73.1	71.2	71.1
P.C. Number	: 1 hr.	1.80	1.06	1.16	1.23	1.53	1.7
	2 hr.	2.30	1.45	1.54	1.63	2.02	2.23
	3 hr.	2.64	1.70	1.87	1.80	2.35	2.51
	4 hr.	2.79	1.82	1.95	1.97	2.49	2.71



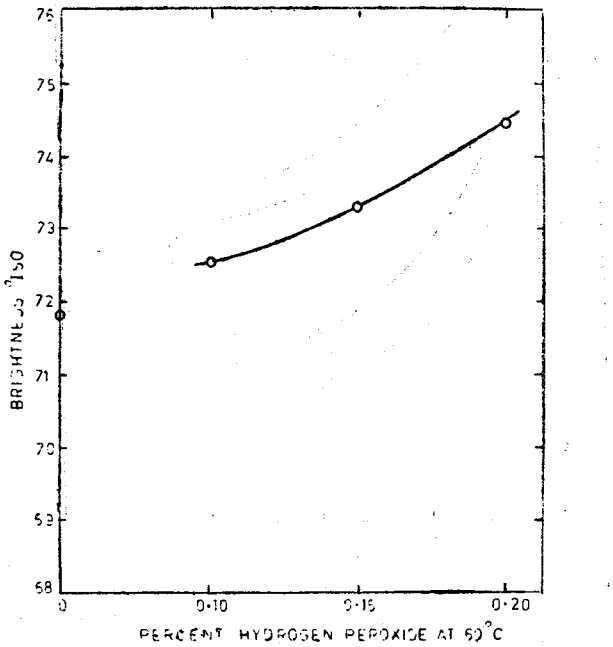
FIG·1 EFFECT OF HYPOCHLORITE ON BRIGHTNESS OF RICE STRAW PULP



FIG·3 EFFECT OF HYDROGEN PEROXIDE ON BRIGHTNESS OF RICE STRAW PULP BLEACHED BY VARIOUS LEVELS OF HYPOCHLORITE



FIG·2 EFFECT OF HYPOCHLORITE ON BRIGHTNESS DROP OF RICE STRAW PULP AFTER AGING

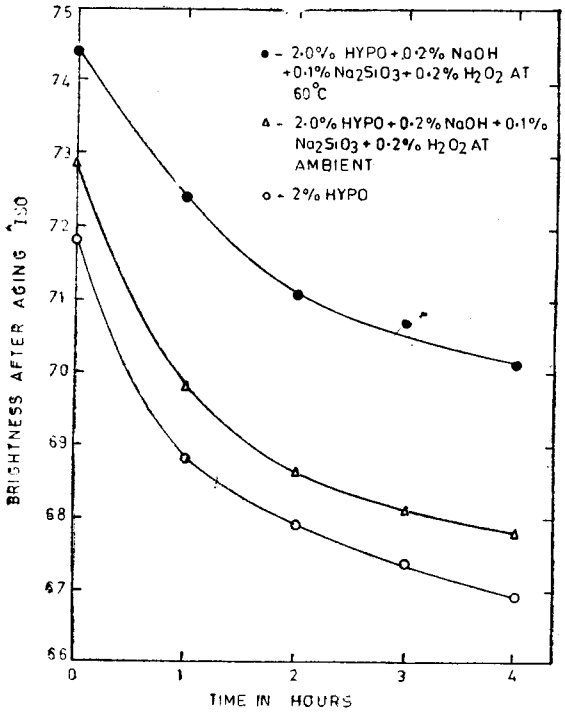


FIG·4 EFFECT OF HYDROGEN PEROXIDE ON BRIGHTNESS DEVELOPMENT OF HYPOCHLORITE BLEACHED RICE STRAW PULP

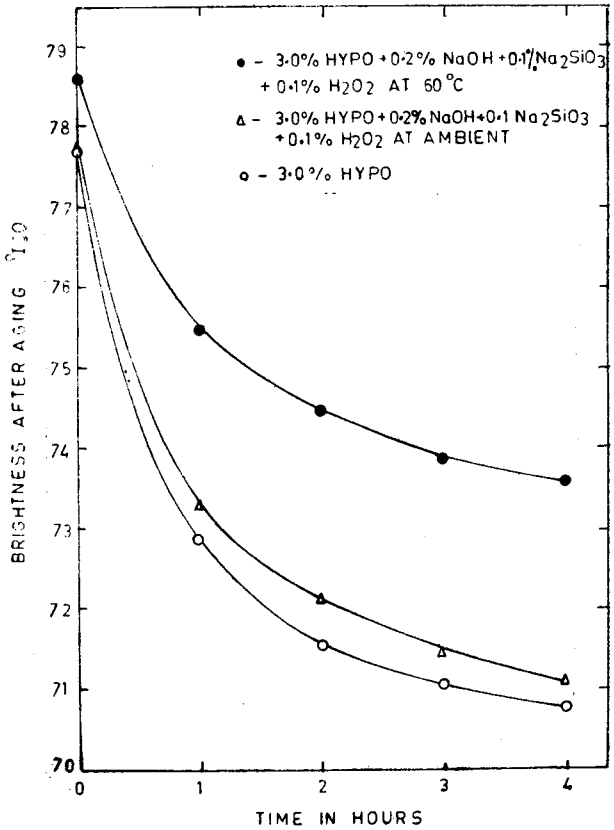
FIG 5 & 6. The chlorinated rice straw pulp was bleached with 2% and 3% hypochlorite and subsequently by 0.2% and 0.1% H_2O_2 (100%) respectively. These plots show that at any moment of time, brightness values on aging are higher for pulp bleached with hypochlorite-peroxide than for the pulp bleached by hypochlorite alone.

5. FIG.7 & 8 show the stability of brightness in terms of post colour number against time of aging. The figures show that at any moment of aging time p.c. number is lowest for the pulp bleached by usage of hydrogen peroxide with proper buffer and stabiliser (caustic and sodium silicate) at elevated temperature. This shows the highest stability of brightness for this pulp. This may be due to formation of perhydroxyl ions in alkaline conditions. These perhydroxly ions cleave the chromophoric groups associated with pulp to render them colourless. The rate of formation of perhydroxyl ions is high at elevated temperature. If peroxide bleaching is carried out without buffer, stabilizer and under ambient conditions immediately after hypochlorite bleaching, there is certainly good rise in brightness value, but the brightness stability is poor. However, final brightness value and stability of brightness is certainly higher than in case of chlorinated straw pulp bleched by usage of calcium hypochlorite alone.

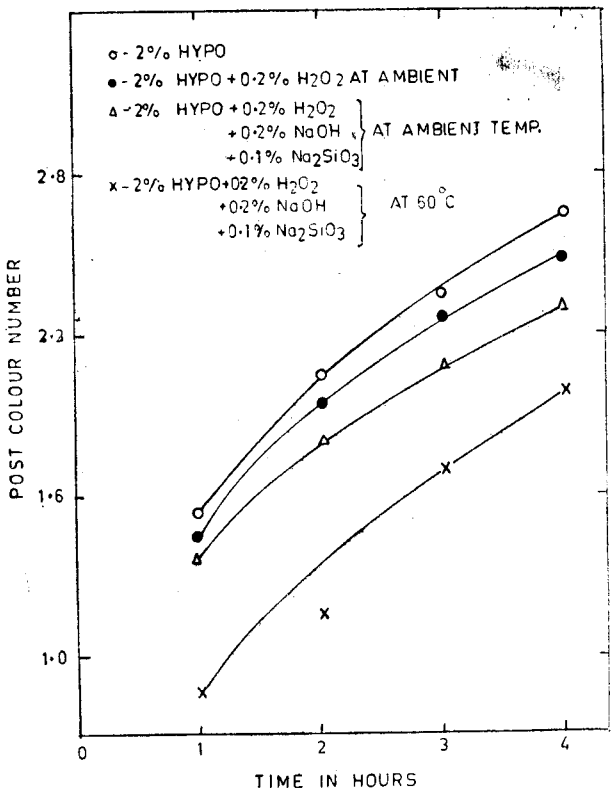
6. It can be seen from FIG 9 that hypochlorite-peroxide bleached chlorinated rice straw pulp is always having higher brighteness values as compared to that of chlorinated rice straw pulp bleached by usage of hypochlorite alone. This is seen even after aging the pulp for four hours.



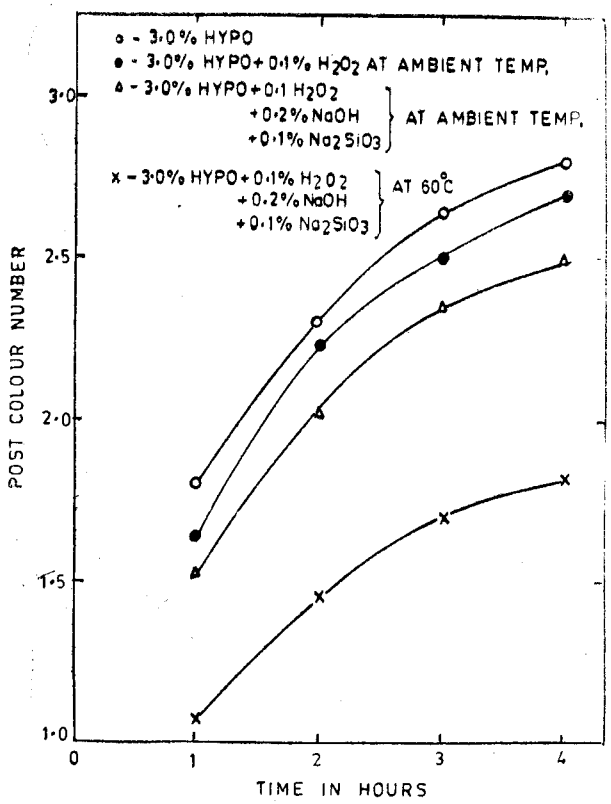
FIG·5 EFFECT OF TEMPERATURE AND BUFFER ON BRIGHTNESS DROP DURING AGING OF RICE STRAW PULP BLEACHED WITH HYDROGEN PEROXIDE



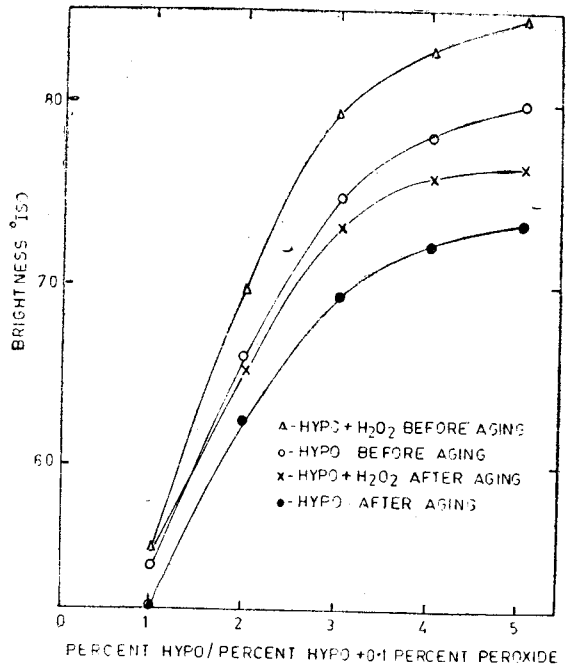
FIG·6 EFFECT OF TEMPERATURE AND BUFFER ON BRIGHTNESS DROP DURING AGING OF RICE STRAW PULP BLEACHED WITH HYDROGEN PEROXIDE



FIG·7 EFFECT OF TEMPERATURE AND BUFFER ON BRIGHTNESS STABILITY OF RICE STRAW PULP DURING PEROXIDE BLEACHING



FIG·8 EFFECT OF TEMPERATURE AND BUFFER ON BRIGHTNESS STABILITY OF RICE STRAW PULP DURING PEROXIDE BLEACHING



FIG·9 EFFECT OF HYPO / HYPO-PEROXIDE ON BRIGHTNESS OF RICE STRAW PULP BEFORE AND AFTER AGING

CONCLUSIONS

Hypochlorite bleached chlorinated rice straw pulp when bleached further by usage of hydrogen peroxide, a pulp with higher brightness value as well as with good brightness stability can be achieved.

Rice straw pulp can be bleached effectively by usage of hypochlorite-hydrogen peroxide in two stages. The brightness values as well as the brightness stability thus obtained are always higher than the pulp bleached by usage of hypchlorite alone.

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