Instrumental and Chemical Process Control in Bleaching of Pulp

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INTRODUCTION

In conventional bleaching systems which use different combinations of C, E, H_1 H_2 P sequences, the ultimate chemical reactions lead to :

a) Delignification
b) Cellulose oxidation
c) Removal of colouring matter
d) Degradation of cellulose molecules
e) Improving the brightness of pulp.

In this paper, the classical chemical reactions of cellulose with Cl_2 and sodium or Calcium Hypochlorite ions as well as reaction with Hydrogen peroxide are discussed in association with the formation of various types of Oxycelluloses and the mechanism of molecular chain degradation, leading to subsequent strength losses and weakening of pulp.

The chemistry and process parameters of Hypochlorite bleach liquors which are ideally suitable for bleaching of pulp are also discussed.

Process parameters such as viscosity, Copper Number and Methylene Blue absorption Number are discussed in relation to the chemical nature of Oxycelluloses produced in bleaching.

Instrumental measurement of Brightness with the International Trichromatic method using a classical spectrophotometers with primary Red—Blue and Green filters is discussed.

A novel approach for Brightness measurement using the Tristimulus Blue Filter and measurement/Computation of Yellowness factor (% yellowness) is described.

Values obtained are also compared with conventional values obtained by using the Post Colour Number formula.

Suitable recommendations for controlling all process parameters in Bleaching and also in measurement of Brightness and Yellowness of the bleached pulps are out lined.

BLEACHING OF PULP

CHLORINATION

The introduction of a Chlorine radical in the Lignin molecule and its subsequent removal through alkali extraction are discussed in Figure 1.

Since this reaction is very specific to lignin and its derivative by and large the cellulose molecules are immune and do not take part in this reaction. However due to the high acidic pH conditions some degradation of cellulose chains may take place during chlorination.

BLEACHING WITH HYPOCHLORITES

The principal ionic distributions of Calcium and Sodium Hypochlorites in aqueous solutions of various pH conditions are shown in Figure 2.

From this it is clearly evident that three distinct species of Chlorine are involved in the bleaching reactions.

a) Chlorine as Cl_2 gas
in the pH range 0.5 to 4.0

b) Hypochlorous Acid HOCl
in the pH range 3.5 to 7.5

c) Hypochlorite ions—OCl
in the pH range 7.0 to 13.5

Further in the same context the relative reaction rates of Cellulose with Hypochlorites at the above pH conditions are also shown in Figure 3.

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From these reactions the following important observations are made :

Fig. 1.

Chlorination and Alkali Extraction Reaction of Lignin

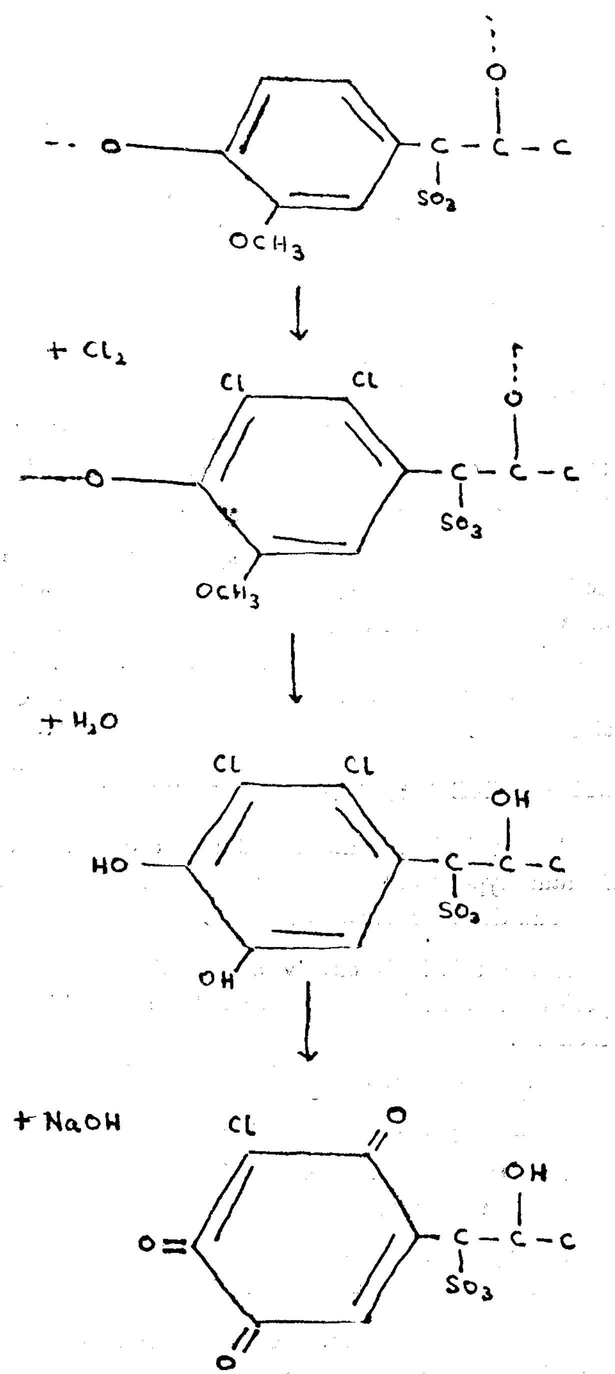


FIG. 2

Distribution of HOCl and OCl⁻ in Hypochlorite Bleach Liquors

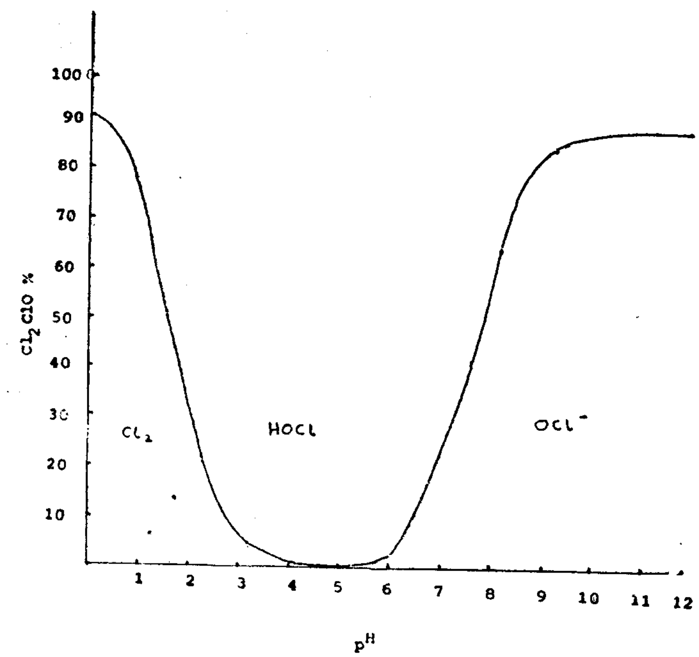
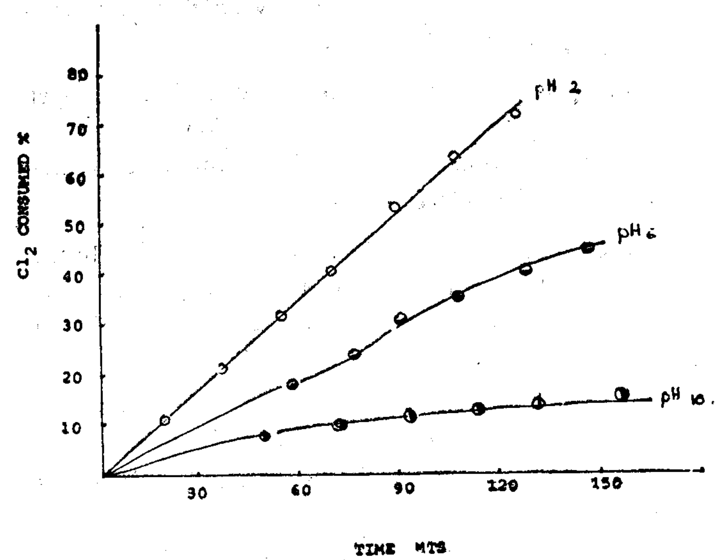


FIG. 3

Chlorine Consumption at Different pH Conditions



a) At very low pH conditions, the bleaching system consists of mainly Cl_2 gas and small quantities of of HCl.

Thus no bleaching occurs and only acidic degradation of the cellulose chain occurs, leading to heavy strength losses and low viscosity pulps,

b) At neutral and near neutral pH range (4.5 to 7.0) bleaching (oxidation) is largely due to HOCl ions and this is also followed by acidic degradation and chain cleavage.

c) In alkaline pH range of 7.5 to 13.0, oxidation and bleaching of cellulose occurs mainly through reaction with OCl, Hypochlorite ions.

However the reaction rate is considerably reduced with subsequent pulps which are less degraded.

Thus in order to obtain a good brightness and strong pulp it is necessary to control the reaction pH in the lower alkaline range (7.0 to 9.5).

Below this pH, although this pulp brightness is high, considerable degradation occurs.

Above this range, in highly alkaline condition oxidation and bleaching are considerably slowed down and the pulp brightness is poor.

TYPES OF OXYCELLULOSES FORMED IN BLEACHING

The general Odixative reactions of cellulose with calcium or sodium Hypochlorite are schematically shown in Figure 4.

The two principal types of Oxycelluloses formed are

a) Reducing Oxycelluloses which contain either an aldehyde or ketonic group.
and

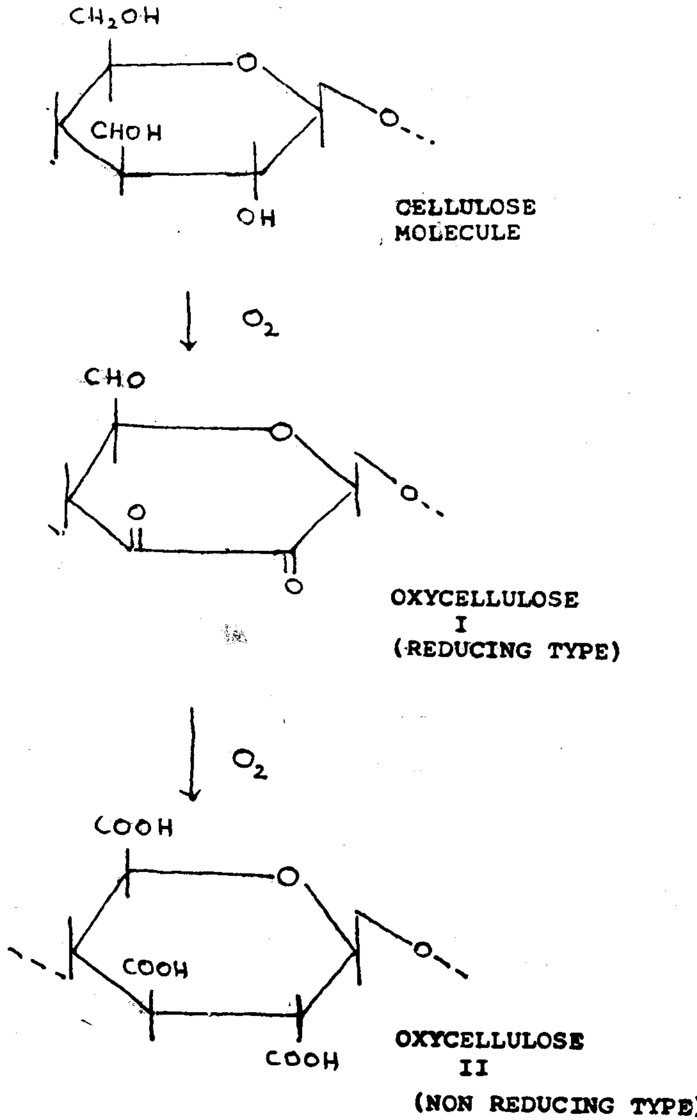
b) Non reducing types which primarily contain the Carboxylic groups.

It is important to note that Reducing type of Oxycelluloses are responsible for causing a reduction in Brightness on exposure to Sunlight and give high Post Colour Number.

Whereas the non reducing types of oxycelluloses are largely obtained through a mild bleaching stage with Hydrogen Peroxide or Chlorine Dioxide as a final bleaching stage and are stable to light and do not cause further yellowing of the pulps.

FIG. 4

Oxycelluloses Formed During Hypochlorite Bleaching of Pulp



Estimation of the Aldehyde/Carbonyl contents of oxycelluloses is usually carried out by *Copper Number* estimations.

Whereas the Carboxylic type of oxycelluloses are estimated by Methylene Blue absorption tests.

These tests are described in detail in Appendix 1.

Thus for obtaining high brightness low P.C. Number pulps which possess good over all strength properties the following critera are important.

1 pH range recommended. 7.5 to 9.5
2 Low Copper number.
3 Medium to Low Methylene Blue absorption number.
4 High viscosity.
5 Low P.C. Number.

Typical Copper Number and Methylene Blue absorption number values are shown in Figures 5 and 6.

MEASUREMENT OF BRIGHTNESS AND YELLOWNESS FACTOR OF BLEACHED PULPS

In most cases measurement of pulp brightness is done on conventional spectrophotometer or Elrepho brightnss meters by using reflectance values at Blue filter (R451).

Post colour number is measured by an accelerated ageing test and using the formula

$$\frac{(1-R_2)^2 - (1-R_1)^2}{2 R_2 R_1} \times 100 = \text{P.C.No.}$$

Where R_2 = Brightness after ageing
R_1 = Initial Brightness

However it is strongly recommended that these parameters should be measured by using the *Trichromatic Colour Measurement* system using Red, Green and Blue filters.

The theory and academise principles of this system have been earlier reported in IPPTA September 1983.

In this system the measurement of Brightness and colour of a smooth surface is done by using three primary filters at.

RED	—	595 n.m.
GREEN	—	557 n.m.
BLUE	—	455 n.m.

(Fig. 6)

These TRICHROMATIC EILTERS are specially produced to international colour standards as per the Optical Society of France and U.S.A. specifications using Oxides and salts of cobalt, Chromium and pure organic pigments.

FIG. 5 Viscosity Vs.Copper No. of Pulp (Bleached)

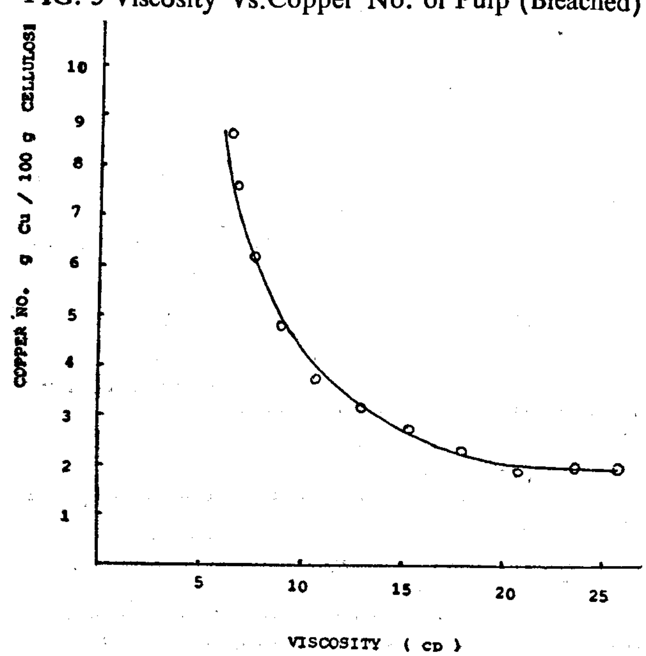
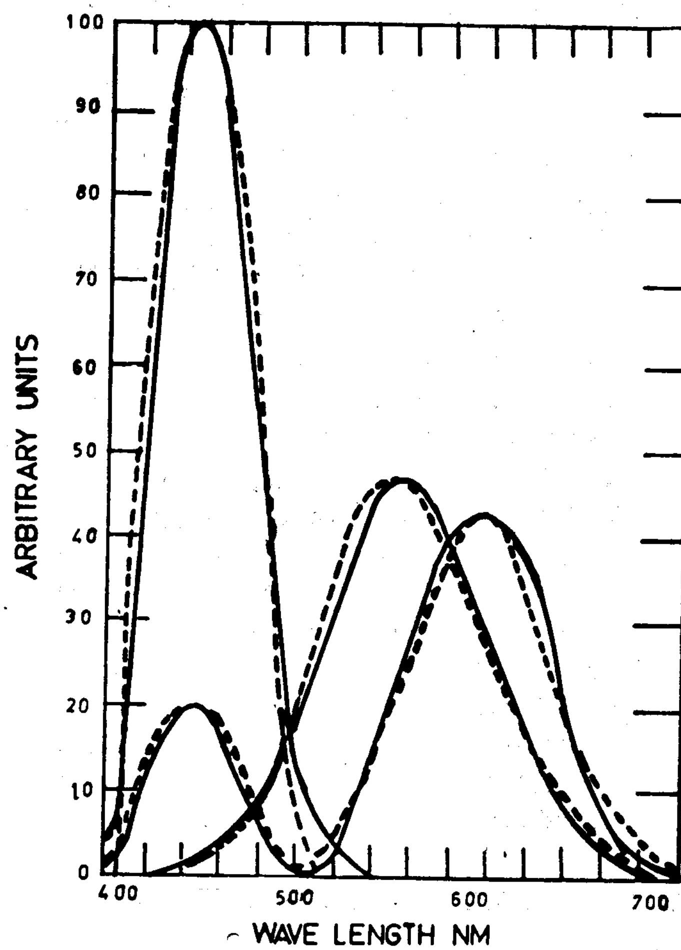


FIG. 6



SPECTRAL CURVES OF TRISTIMULUS FILTERS.

APPENDIX–I

1) **Copper No. of pulp, paper and paperboard**
TAPPI STANDARD—T 430 OS—75.

Definition

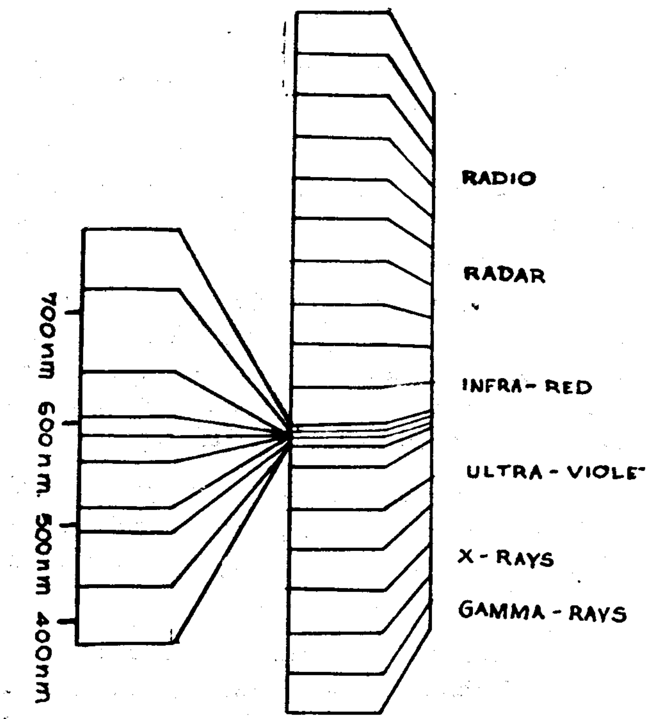
Copper number is defined as metallic copper (in Cu_2O) resulting from the reduction of $CuSO_4$ by 100 gms of the pulp or paper fibres.

2) **Methylene blue absorption test**
Definition

Number of milli moles of Methylene blue absorbed per 100 gms of cellulose under standard conditions of the test.

This test is used for the estimation of carboxylic acid groups.

FIG. 6 (a)



DISTRIBUTION OF SUN'S RAYS SPECTRUM

Reflectance values obtained through these filters are called

R	=	X Tristimulus Red
G	=	Y Tristimulus Green
B	=	X Tristimulus Blue

These values are then converted to *Trichromatic Co–efficients* X, Y and Z such that

$$X = \frac{X}{X+Y+Z}$$

$$Y = \frac{Y}{X+Y+Z}$$

$$Z = \frac{Z}{X+Y+Z}$$

Thus $X+Y+Z = 1$

The advantage of using the Trichromatic method is that any colour or white object can be accurately measured and specified through its X, Y and Z co–efficients.

Further it is only necessary to obtain the X and Y co–ordinates, since Z can be obtained as $Z = 1 - (X + Y)$.

Thus the X, Y co–ordinates of any colour can be graphically plotted and the position of such a colour can be accurately located on the graph. This system further helps in obtaining accurate colour matchings of a white or coloured object.

It is interesting to note that even a highly bright/white object has three RGB coefficients.

Thus	X	=	0·33
and	Y	=	0.33

All colours and white objects have been thus computed by this method to represent what is known as the colour triangle (Figure7).

The use of this colour triangle helps in analysing various factors and parameters in colour and brightness measurements e.g.

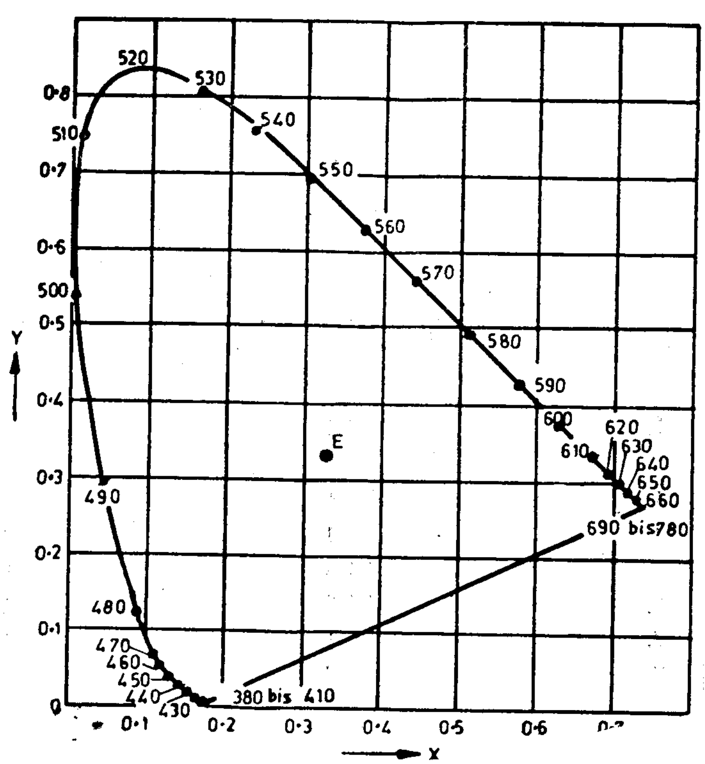
a) Determination of specifie colour wave length and intensity or depth of a colour.

b) Purity of colour.

c) Accurate shade/colour matching.

d) Accurate comparison of white or bright objects. (This is difficult on ordinary brightness meters).

FIG. 7



THE C.I.E. COLOUR TRANGLE

e) Measurement of Yellowness factor.

f) Determination of complimentary wave length of any colour.

g) Quick analysis of Secondary and Tertiary colours.

This method also gives a rapid estimation of % Yellowness of any bleached pulp by using the equation

$$\% \text{ Yellowness} = \frac{R - B}{G} \times 100$$

$$\text{or} \quad \frac{X - Z}{Y} \times 100$$

APPLICATION OF TRICHROMATIC COLOURIMETRY IN MEASUREMENT OF BLEACHED PULP

1-BRIGHTNESS MEASUREMENTS

Several bleached pulps have been analysed by this method for obtaining the % Brightness using the Trichromatic Blue filter instead of the conventional R 451 filter used in Elrepho/spectrophotometers.

Very close correlationship has been obtained in the two sets of values. (Table 1).

This is easily explained since the Trichromatic Blue filter has a peak wave length at 455 nm which is very near the R 451 nm.

Thus it is recommended that % brightness measurements be carried out with the Trichromatric Blue filter.

2-CORRELATION BETWEEN % YELLOWNESS AND P.C. NUMBER

For measurement of the P,C. Number as mentioned earlier, the bleached pulp are subjected to an acclerated aging process and then examined for initial and final brightness values R_1 and R_2.

It has been observed that the % yellowness of bleached pulps as obtained by the earlier formula simplifies the method considerably, since the values of Trichromatic Green filter represent to a large extent the yellow/green component in the bleached pulps.

It is interesting to note that although bleached pulps uisually appear white/bright, they contain a sizable fraction of yellow colour component which can not be estimated by the R 451 filter.

On the other hand the green and red components obtained by Trichromatic method easily give a measure of this yellow fraction which is ultimately responsible for P.C. Number.

Table 2 gives the correlationship obtained by using this method, between % yellowness and P.C. Number.

TABLE—1

Percent Reflectance Values of Bleached Pulp Sheets Using The R 457 And Tristimulus Filters

Sl. No.	Initial Brightness (R 451)	'A' FMX	'G' FMY	'B' FMZ
1.	77.4	892	87.1	76.4
2.	80.5	91.1	89.3	79.8
3.	80.1	89.8	88.7	80.0
4.	82.1	90.7	89.3	81.4
5.	83.6	91.7	90.4	83.0
6.	84.6	92.0	90.8	84.2
7.	85.1	91.7	90.7	84.4
8.	85.3	91.9	90.7	84.9

TABLE—2

Relationship Between P.C. No. And Percent Yellowness

Sl. No.	Brightness Before Ageing %	Brightness After Ageing %	P. C. No.	Yellowness Before Ageing% 'M'	Yellowness After Ageing% 'N'	Increase in percent yellowness after ageing%(N–M)=y
1.	77.4	63.2	7.42	14.69	22.10	7.41
2.	80.5	62.6	8 78	12.65	22.44	9.79
3.	80.1	61.6	9.41	11.04	23.67	12.63
4.	82 1	61.0	10.52	10.41	22.70	12.29
5.	83 6	57.3	14.30	9.62	25.70	16.08
6.	84.6	56.6	15.23	8.59	27.77	19.18
7.	85.1	55.6	16.53	8.04	28.41	20.37
8.	85.3	55.1	17.03	7.71	29.07	21.36

ADVANTAGES OF USING HYDROGEN PEROXIDE AND CHLORINE DIOXIDE IN BLEACHING OF PULPS

It is observed that incorporation of a final H_2O_2 or ClO_2 stage improves the stability of Brightness to ageing since the C.H.O. (Aldehydic) and C = O (Ketonic) groups produced in Hypochlorite Bleaching are rapidly converted to COOH (Carboxylic) groups, which are more stable to light discolouration.

Such pulps may exhibit a medium to high Methylene Blue Absorption value.

RECOMMENDATIONS

Thus in summing up, the following important proeess control parameters need close monitoring in the bleaching and analysis of bleached pulps.

1) Control of pH in the range of 7.5 to 10.0.
2) Medium to High Viscosity.
3) Low Copper number.
4) Medium to Low Methylene blue absorption number.
5) Brightness measurement by the Trichromatic method.
6) % Yellowness or Yellowness Factor to obtain a rapid estimation of P.C. Number.
7) Close control of Brightness matching between lots and batches by use of x and y coordinates.
8) Use of a final stage H_2O_2 or ClO_2 bleaching considerably reduces the P.C. Number and imparts Brightness stability.

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