

Peracetic Acid Oxidation of Semi Bleached Pulp of Eucalyptus Grandis and Brightness Changes During Bleaching

MOHAN RAO N.R.*, GUHA, S.R.D.**

ABSTRACT

Semi bleached soda pulp was prepared by bleaching with CE-H sequence to a brightness of 74% ISO. Peracetic acid oxidation of semi bleached pulp was carried out with varying concentration of peracetic acid (from $20 \times 10^{-4} M$ to $0 \times 10^{-4} M$), consistency (2 and 3%), temperature ($25^{\circ}C$ to $40^{\circ}C$) and pH (7 and 8). The reaction was found to follow first order kinetics. Reaction rate increased with pH and doubled for every 10° rise in temperature. The brightness development improved with peracetic acid concentration and also pH. Use of 0.304 g/l concentration of peracetic acid (1.5% on pulp) resulted in brightness increase of 7-8 units by keeping pH 7-8 and temperature $30-35^{\circ}C$ for two hours.

Introduction :

Peracetic acid has been shown to be an effective pulp bleaching agent (1, 2) although it has not yet been accepted commercially for this purpose mainly because of its cost. Kraft pulp can be bleached to 80-85% brightness at moderate temperatures in a short time without being limited by topochemical factors (2). Peracetic acid has been used as a bleaching agent in the final stage for chemical pulp (3 to 5) and has been compared with chlorine as delignifying agent and with sodium hypochlorite and chlorine dioxide as brightening agents on kraft and sulfite pulps (6). Rapson W.H. (7) has shown that chlorine dioxide and peracetic acid may be used together for bleaching pulp. Higher brightness is achieved than with either bleaching agent alone.

Experimental :

i Preparation of Semi bleached soda pulp :

Soda pulping of Eucalyptus grandis was carried out in a series digester consisting of six stainless steel bombs each of 2.5 litres capacity rotating in an electrically heated poly ethylene glycol bath. At the end of the cooking period, the bombs were taken out, cooled in a water bath, contents filtered on a muslin cloth and

washed thoroughly. The cooking conditions and results are as below.

Sodium hydroxide Na_2O %	= 18.0
Chips to liquor ratio	= 1 : 3
Cooking temperature $^{\circ}C$	= 170
Cooking time Min	= 120
Screened pulp yield %	= 51.5
Kappa number of the pulp	= 21.5

The above pulp was bleached by C-E-H sequence to a brightness of about 74% ISO. The bleaching conditions and results are given in table 1.

The bleached pulp was treated with sulphur dioxide to improve the pulp cleanliness and brightness stability, under the following conditions.

Pulp Consistency %	= 2.0
Temperature	= Ambient
Time Min	= 15
pH	= 4

**Retired Director, Forest Products Research, Forest Research Institute and Colleges Dehradun.

Presently Professor of B. N. Degree College Dandeli (Karnataka).

*Presently Chief Chemist, Tamil Nadu Newsprint and Papers Ltd. Velayuthamplayam (P.O.), Tamil Nadu.

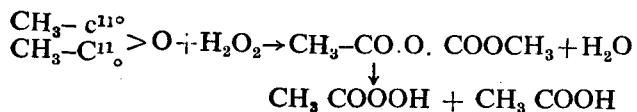
TABLE-1
BLEACHING OF EUCALYPTUS GRANDIS PULP

Kappa number of the pulp	: 21.5		
Chlorination :			
Chlorine applied/consumed on pulp %	: 4.75/4.53		
Final PH	: 2.0		
Alkali extraction :			
NaoH applied %	: 1.75		
pH Initial/Final	: 10.8/10.5		
Hypochlorite stage :			
Hypochlorite as Cl ₂ applied/consumed%	: 1.40/1.17		
Buffer used as NaoH %	: 0.42		
Total chlorine applied/consumed %	: 6.15/5.70		
Total NaoH applied %	: 2.17		
Brightness of bleached pulp %ISO	: 74.6		
Bleaching conditions :			
	Chlorination	Alkali extraction	Hypochlorite stage
Consistency %	3.0	8.0	8.0
Temperature °c	30	60	40
Time .min	30	60	120
pH maintained	about 2.0	above 10.0	above 9.0

The above bleached pulp was taken for kinetic studies.

ii Preparation of Peracetic Acid :

Peracetic acid was prepared in the Laboratory by reacting Acetic Anhydride with Hydrogen Peroxide in ammonical medium at low temperature under controlled conditions.

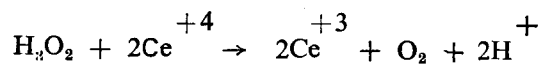


A three-neck flask equipped with a stirrer and a dropping funnel was immersed in a water bath maintained below 15°C. The flask was filled with 850ml deionised water, 52ml of 25% ammonia and 45ml of 30% Hydrogen Peroxide. 50ml of Acetic Anhydride was added dropwise slowly into the reaction flask with vigorous stirring. Dropping time of about 15 minutes was allowed and the reaction temperature was kept below 30°C during addition of Acetic Anhydride. Stirring was continued for another one hour. The solution was allowed to stand overnight in a fridge. Though

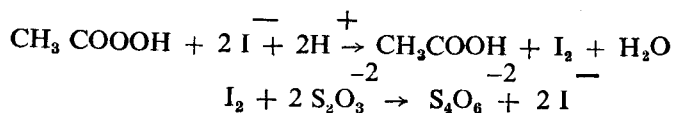
the volume of water could be changed, the molar ratio of Acetic Anhydride to Hydrogen Peroxide was always maintained constant at 1.50 to 1 : 25 : 1

iii Analysis of Peracetic Acid :

Peracetic acid, contains some Hydrogen Peroxide which can be titrated in presence of Peracetic acid in an acid solution with cerium sulfate.



When the titration is conducted in acid and cold solution Peracetic acid is not decomposed into peroxide. The consumption of cerium sulfate is directly proportional to the peroxide concentration. After cerium sulfate titration a conventional iodometric titration is carried out to determine the amount of Peracetic acid.



Peroxide :

Crushed ice was added into 150 ml of dilute sulfuric acid (5%) to keep the temperature below 10°C. When this temperature had reached 10 ml of stock solution was added and titrated with 0.1N ceric ammonium sulfate from 10 ml microburette using Ferroin indicator. At the end point the colour turned from red to pale blue. Titrant Vol : V₁

Peracetic Acid :

After the titration of Peroxide, 10 ml of Potassium Iodide was added into the above solution and three drops of ammonium molybdate solution was added and the liberated iodine was titrated with 0.1N thiosulfate using starch as indicator.

Titrant volume : V₂

$$\text{Concentration of Peroxide g/l} = \frac{V_1 \times n_1 \times 17}{a}$$

V₁ : Titrant volume, ml

n₁ : Normality of ceric ammonium sulfate

a : sample volume, ml

17 : Equivalent weight of H₂O₂

$$\text{Concentration of Peracetic acid g/l} = \frac{V_2 \times n_2 \times 38}{a}$$

V₂ : Titrant volume, ml

n₂ : Normality of thiosulfate solution

a : sample volume, ml

38 : Equivalent weight of Peracetic acid.

Peracetic acid, prepared by the above method has the following concentration.

Peracetic acid g/l = 35-40

Hydrogen Peroxide g/l = 0.5 and below

On long standing, Peracetic acid loses active oxygen and H_2O_2 concentration also increased. So, Peracetic acid was prepared every time one day prior to the kinetic studies, in small batches, always keeping the molar ratio of Acetic Anhydride to Hydrogen Peroxide constant and analysis of the solution was carried out before taking for kinetic experiments. As the H_2O_2 content, by this method, was quite negligible, peracetic acid was taken as free from H_2O_2 for our practical purposes.

iv Oxidation studies of semi bleached soda pulp

Accurately weighed quantity of semi bleached pulp (6 gm on oven-dry basis) was soaked overnight and then disintegrated & filtered on a buchner funnel, recirculating the filtrate to prevent loss of fines. The wet weight of the pulp was taken and then diluted, with requisite water so that after the addition of buffer and peracetic acid, the total volume would be 300 ml. pH of the reaction mixture was tested periodically by dipping the pH meter electrode into the reaction mixture. pH was maintained during the kinetic studies with in Sodium hydroxide or 1N Hydrochloric acid.

The concentration of residual Peracetic acid was determined iodimetrically. 5 ml aliquot was pipetted out into a conical flask containing 150 ml of 5% sulfuric acid. 10 ml 10% potassium iodide and three drops of 3% Ammonium Molybdate were added. The liberated iodine was titrated with 0.009N thiosulfate solution using starch indicator towards the end point. In this way, aliquots of the reaction mixture were titrated at appropriate time intervals and from these data concentration of residual Peracetic acid was calculated. At the end of the reaction time the bleached pulp was washed and then subjected to optical studies. Under the experimental conditions, it was observed that the bleached pulp was always present in sufficient excess and the order of the reaction with respect to Peracetic acid was therefore established from the change in Peracetic acid concentration along with time.

v Preparation of brightness sheets :

2 gm OD pulp was diluted with 400 ml deionised

water, disintegrated in a Laboratory pulp blender and then filtered. The pad was then pressed using 5Kg/cm² pressure for 2 min. using press. Then the sheet was airdried.

vi Measurement of brightness and post colour number :

a. Brightness :

Brightness was measured using Elrepho Reflectance Photometer at 457 nm and results were expressed as %ISO units according to ISO DIS 3688.

b Post Colour Number :

The pulp pad after initial brightness measurement was kept hanging in a forced air circulation oven at $150 \pm 3^\circ C$ for 4 hours without keeping any other specimen in the oven. Post colour number was calculated using the following formula.

$$\text{Post Colour Number} = \frac{100 (1-R'_\alpha)^2}{2R'_\alpha} - \frac{(1-R_\alpha)^2}{2R_\alpha}$$

Where R_α : Diffuse reflectance before aging

R'_α : Diffuse reflectance after aging

Results and discussions :

1. Analysis of Kinetic Data :

The Kinetic data was analysed by following the method of integration. The reaction rate data for Peracetic acid consumption were tested for possible compliance with reaction rate equation for first, second and third order reactions. The reaction was confirmed to be of first order with respect to Peracetic acid concentration over almost all the reaction period and at all pH levels considered in this study.

If the reaction is of first order, the rate of concentration change with time $\left(\frac{dc}{dt}\right)$ should satisfy the following equation :

$$\frac{-dc}{dt} : KC$$

Where K is the first order rate constant which is also known as the specific rate and the rate coefficient. 'C' represents the concentration at any time 't'. The first order rate equation, in its integrated form may be expressed as :

$$K = \frac{2.303}{t} \log_{10} \frac{C_0}{C_0 - X}$$

Where C_o = initial concentration of Peracetic acid

$(C_o - X)$ = concentration of Peracetic acid at any time 't' or residual Peracetic acid.

$$\log_{10} C_o - X = \frac{-K.t}{2.303} + \log_{10} C_o$$

In a first order reaction, a straight line is produced when logarithm of the residual Peracetic acid concentration is plotted against time. The slope of this line will be equal to $-K/2.303$ from which first order reaction rate 'K' can be calculated.

The effect of the following variables have been studied within the limits specified on the rate of reaction of semi bleached pulp and peracetic acid

- Peracetic acid concentration was varied from 20×10^{-4} to 80×10^{-4} M as the lignin content of the bleached pulp is very low (0.85%)
- Pulp consistency (2 and 3)
- Temperature (25°C to 40°C)
- pH was kept at 7 & 8 as the rate of reaction at pH 4 and 5 were low.

i) **Effect of Peracetic and concentration on reaction rate :**

To study the effect of initial peracetic acid concentration on the reaction rate, the kinetic studies were carried out at pH 7 and 8 using different concentration of peracetic acid varying from 20×10^{-4} to 80×10^{-4} M. The effect of peracetic acid concentration on reaction rate at pH 8 is shown in Figure 1.

The plot of logarithm of residual peracetic acid concentration versus time of the reaction gives a straight line correlation at pH 8 and at different initial concentration of peracetic acid. This indicated that oxidation of semi bleached pulp follows first order kinetics with respect to peracetic acid concentration.

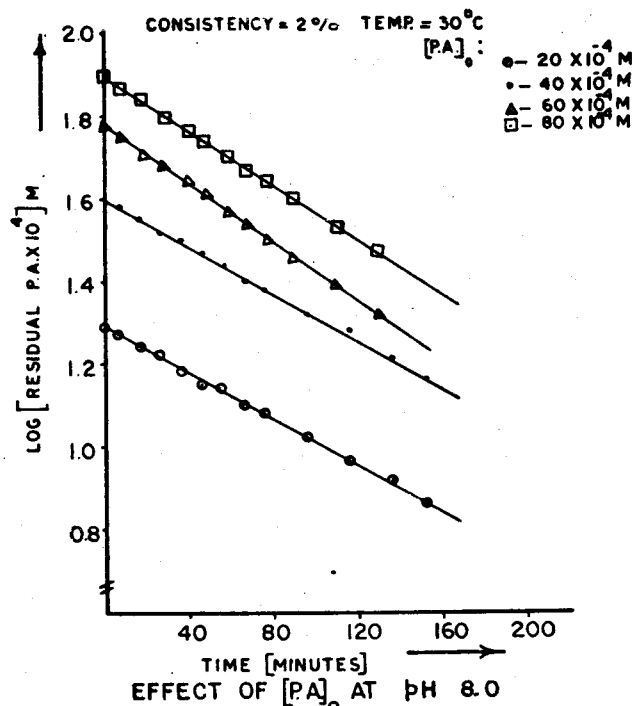


FIG.—1

- ii) **Effect of Consistency on the reaction rate :**
To study the effect of consistency on reaction rate, studies were carried out at pH 7 and 8 and the consistency 2% to 3%. The effect of consistency on reaction rate at pH 7 is shown in Figure 2.

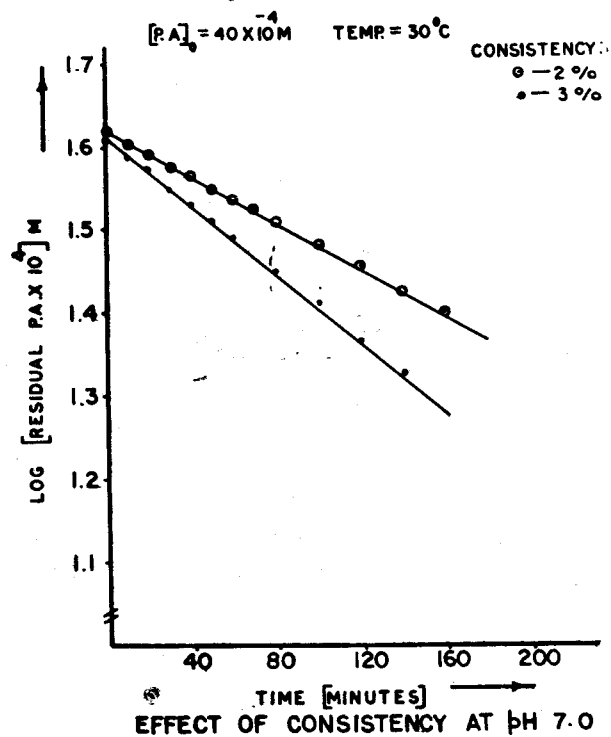


FIG.—2

A straight line correlation is obtained when logarithm of residual peracetic acid was plotted against time at 2% and 3% consistency. First order velocity increased with increasing consistency.

iii) **Effect of temperature on the reaction rate :**

To study the effect of temperature on the rate of reaction, kinetic studies were carried out at different temperatures ranging from 25°C to 40°C. The summary of results is tabulated in table 2 and a typical graph presented in figure 3.

TABLE—2
EFFECT OF TEMPERATURE ON REACTION RATE

Temperature	pH	$k \times 10^4 M$
25	7	20.2
30	7	33.1
35	7	43.2
Temperature		Coefficient : 2.1
25	8	48.9
30	8	67.2
35	8	84.9
40	8	134.3
Temperature		Coefficient : 1.9

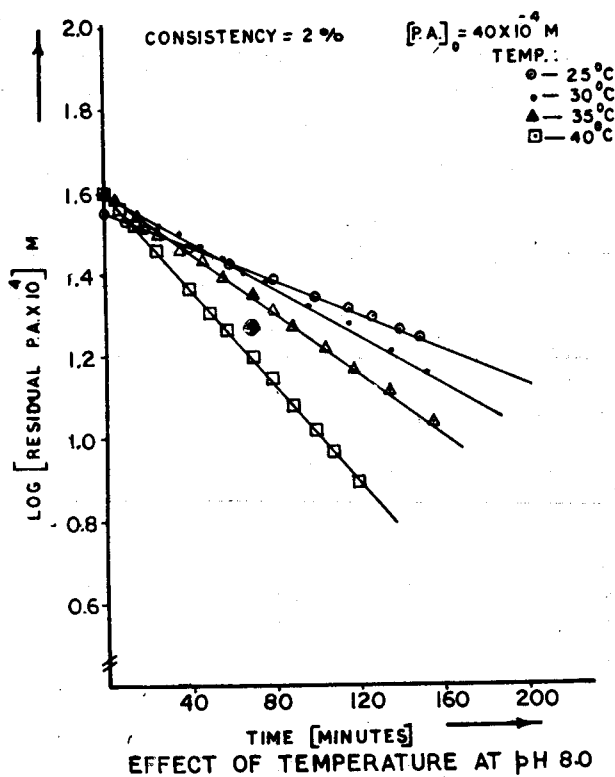


FIG. 3

It can be observed that increase in temperature increased the rate of first order reaction at pH 7 and 8 studied and the first order velocity constant increases nearly two times for every 10° rise in temperature, the temperature coefficient $\frac{k_{t+10}}{K_t}$ being nearly 2.0.

iv) **Effect of pH on reaction rate :**

Effect of pH (7 and 8) at different temperatures, peracetic acid concentration at $40 \times 10^{-4} M$ and 2% consistency is shown in table 3.

TABLE—3
EFFECT OF pH ON REACTION RATE
Peracetic acid concentration = $40 \times 10^{-4} M$
consistency = 2%

Temperature	pH	$k \times 10^4 \text{Min}^{-1}$
25	7	20.2
25	8	48.9
30	7	33.1
30	8	67.2
35	7	43.2
35	8	84.9

The rate constant increased with pH. The same trend is observed with different peracetic acid concentrations also.

2) **Brightness changes in Semi bleached pulp :**

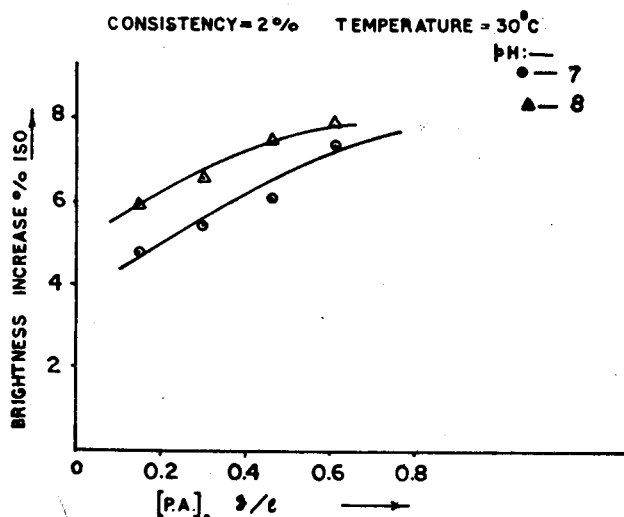
Initial brightness of the CEH bleached pulp was 74.6% ISO and post colour number was 2.0.

1) **Effect of Peracetic acid concentration on brightness :**

Peracetic acid concentration was varied from 0.152 g/l to 0.608 g/l (0.76% to 3.04% on pulp) and at pH 7 and 8 and keeping the temperature at 30°C and consistency at 2%. Bleaching time of 180 minutes or time for almost complete exhaustion of peracetic acid, whichever was earlier, was given for each run. Results are given in table 4 and represented graphically in figure 4.

TABLE—4
EFFECT OF PERACETIC ACID CONCENTRATION ON BRIGHTNESS

Consistency = 2%		Temperature : 30°C		
Peracetic acid concentration g/l	Peracetic acid % on pulp	pH	Increased in brightness (%ISO)	Post colour number
0.152	0.76	7	4.8	1.5
0.304	1.52	7	5.4	2.1
0.456	2.28	7	6.1	2.1
0.608	3.04	7	7.4	1.4
0.152	0.76	8	5.9	1.7
0.304	1.52	8	6.6	2.0
0.456	2.28	8	7.5	1.7
0.608	3.04	8	7.9	1.8



EFFECT OF PERACETIC ACID CONCENTRATION ON BRIGHTNESS IN SEMI-BLEACHED SODA PULP

FIG.—4

It can be observed from table 4 and fig 4, that brightness increased with peracetic acid concentration. Brightness development at lower concentration of Peracetic acid is more. In the later investigations only 0.30 g/l (1.52% on pulp) Peracetic acid was used. Post colour number remains the same with increase in concentration of Peracetic acid, showing that brightness stability is unaffected.

2) Effect of Temperature on brightness :

Effect of temperature on brightness was studied at temperatures ranging from 25°C to

40°C and keeping the concentration of peracetic acid constant at 0.30 g/l and consistency at 2%. The results are summarised in table 5.

TABLE—5
EFFECT OF TEMPERATURE ON BRIGHTNESS

Temp. °C	pH	Bleaching Time min	Brightness increase (% ISO)	Post colour number
25	7	180	6.3	1.9
30	7	180	5.4	2.1
35	7	180	6.2	1.1
40	7	160	6.9	1.8
25	8	180	7.2	1.9
30	8	160	6.6	2.0
35	8	160	7.9	1.0
40	8	120	8.3	1.6

Though temperature has got no significant effect on improvement of brightness, the bleaching time can be reduced at higher temperature.

3) Effect of pH on brightness :

The effect of pH on brightness was studied at 7 and 8, with increasing peracetic acid concentration at 2% consistency, at 30°C and also at different temperatures with 0.76 g/l peracetic acid and 2% consistency.

The results are presented in tables 6 and 7.

TABLE—6
EFFECT OF pH ON BRIGHTNESS (AT DIFFERENT CONCENTRATIONS OF PERACETIC ACID)

Consistency ; 2%		Temperature : 30°C	
Peracetic acid concentration g/l	pH	Increase in brightness (% ISO)	Post colour number
0.152	7	4.8	1.5
0.152	8	5.9	1.7
0.304	7	5.4	2.1
0.304	8	6.6	2.0
0.456	7	6.1	2.1
0.456	8	7.5	1.7
0.608	7	7.4	1.4
0.608	8	7.9	1.8

TABLE-7
EFFECT OF pH ON BRIGHTNESS (AT
DIFFERENT TEMPERATURES)

Consistency : 2%		Peracetic acid concentration=0.304g/l	
Temperature °C	pH	Increase in brightness (% ISO)	Post colour number
25	7	6.3	1.9
25	8	7.2	1.9
30	7	5.4	2.1
30	8	6.6	2.0
35	7	6.2	1.1
35	8	7.9	1.0
40	7	6.9	1.8
40	8	8.3	1.6

From tables 6 and 7 it can be observed that brightness increased marginally when pH is increased from 7 to 8 at all concentrations of peracetic acid and temperatures studied. Post color number of the pulp is unaffected.

Conclusions :

- 1) The linear relationship between the logarithm of residual peracetic acid and time shows that reaction of peracetic acid with semi bleached pulp follows first order kinetics at pH 7 and 8 studied.
- 2) The value of first order velocity constant increases when consistency is increased from 2% to 3%.
- 3) The first order reaction rate increased nearly two times for every 10° rise in temperature at pH 7 and 8 studied.

- 4) The first order reaction rate increased with pH.
- 5) Brightness increased with peracetic acid concentration at the levels studied viz. 0.152 g/l to 0.608 g/l. Rate of Brightness development with lower concentration of peracetic acid is more. With 0.30 g/l peracetic acid (1.52% on pulp) a brightness gain of 5-6 points can be obtained at pH 7 and at 30°C.
- 6) Rate of reaction of peracetic acid with the semi bleached pulp was lower than groundwood pulp.
- 7) Increasing the temperature from 25°C to 40°C has insignificant effect on brightness improvement though it reduces the bleaching time.
- 8) Using 0.30 g/l concentration of peracetic acid (1.52% on pulp) brightness of CEH bleached pulp can be increased by 7-8 units by keeping pH 7-8 and temperature 30-35°C for 2 hours.

References :

1. Stevens, W.R., and Marton, R. Tappi, 49 (10), 452 (1966)
2. Kono, M., and Kondo, T., J. Japan Tappi, 19, 347 (1965)
3. Christiansen, C.B., Burroway, G.L., and Parker, W.F., Tappi 49 (2), 49 (1966)
4. Rapson, W.H., Tappi, 39, 284 (1956)
5. Hatch, R.S., 'The bleaching of pulp' TAPPI Monograph No. 10, New York, TAPPI, 1953, P 106
6. Bailcy, C.W., and Dence, C.W., Tappi, 49 (1), 9 (1966)
7. Rapson, W.H., and Strumula G.B., 'The Bleaching of Pulp' Third Edition, TAPPI Press 1979, P 150.