

Studies on the reaction kinetics and brightness changes during alkaline peroxide oxidation of NSSC pulp isolated from depithed bagasse

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INTRODUCTION

The present shortage of raw materials and growing quality consciousness diverted the attention of pulp and paper technologists to high yield pulp and development of process control parameters, so as to produce specified end products without appreciable impairment in properties. Since most of lignin present in bagasse in neutral sulphite semi chemical pulping is sulphonated, it has a tendency to solubilize and get removed during chlorination during the initial stages of conventional bleaching. The large amounts of the bleaching chemicals, which are required, cause considerable reduction in pulp yield and this make NSSC pulp bleaching an expensive process. Furthermore, most of the non-wood pulps are prone to colour reversion particularly when CEH or CEHH sequences are adopted for bleaching. Neutral sulphite semi chemical pulp made from hardwoods are amenable to peroxide oxidation, essentially when groundwood conditions are applied. Peroxide oxidation of NSSC pulp, involving high consistency and down flow tower was reported in Italy (Anon 1966). Grangaard (1969) suggested much improvement in brightness during peroxide oxidation by making use of pretreatment of pulp with sodium sulphite. The favourable effect of sodium sulphite on brightness following refining was also observed by Hagglund and Lindstorm (1985). The improved brightness resulting from sodium sulphite was partially retained in subsequent refiner bleaching of the chemi mechanical pulp with 2 percent peroxide (Eriksen and Oksum 1980). In peroxide oxidation, stabilization of hydrogen peroxide plays a very important role. In the present study magnesium sulphate-sodium silicate stabilizing agents were

used, following Burton (1986), to achieve hundred percent peroxide stability.

In the following paragraphs reaction kinetics and brightness changes during peroxide oxidation of NSSC pulp isolated from depithed bagasse have been investigated. An attempt has been made to correlate the kinetics data with brightness increase of the pulp.

EXPERIMENTAL

Depithing of Bagasse

Sugarcane bagasse (*Saccharum officinarum*) bales, obtained from Doiwala sugar mill, Dehra Dun, were hammered, screened on a vibratory screener to remove the pith. Partially depithed bagasse was then disintegrated with water to remove remaining pith, dirt and water soluble materials and collected from the water suspension manually. The wet depithed bagasse was air dried and stored for further studies.

Preparation of Neutral Sulphite Semi Chemical Pulp

Neutral sulphite semi chemical pulp was prepared by digesting depithed bagasse in the laboratory autoclave of 25 litres capacity under controlled conditions of 15 percent total chemicals (sodium sulphite and sodium carbonate, 4:1), bath ratio (1:5) at 162° C for 150 minutes (including 60 minutes to raise to maximum temperature)

After digestion, the softened bagasse was refined in Sprout Waldren Disc Refiner (30cm) using the clearan-

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ces of 10, 5 and 2 micron sequentially. Refined pulp was screened in Lambert Screener of 35/100 mm slot width to remove the rejects. Pulp yield and rejects were estimated. The handsheets of the screened pulp were prepared and stored for further studies.

Analysis of Neutral Sulphite Semi Chemical Pulp

The screened neutral sulphite semi chemical pulp was analysed for its kappa number and klason lignin content by adopting TAPPI standard methods, T 236 m-60 and T222 OS-74 respectively.

Progress of Reaction Between Hydrogen Peroxide and Neutral Sulphite Semi Chemical Pulp :

The accurately weighed quantity of NSSC pulp (even dry basis) was mixed with 200 ml distilled water and stirred vigorously for 15 minutes to separate the fibres and to convert it to a uniformly hydrated slurry. The oxidant i.e. hydrogen peroxide reaction mixture was prepared by systematically dissolving sodium silicate (4 percent on o. d. pulp basis) into the dilute solution of magnesium sulphate (0.05 percent on o.d. pulp basis) followed by the addition of estimated quantity of hydrogen peroxide solution so that a solution of required hydrogen peroxide concentration and pH was obtained.

The uniformly hydrated pulp slurry and oxidant, both were thermostate separately. After attaining the required temperature, both were mixed and allowed to react under controlled conditions of pH and temperature with continuous mixing in a four necked round bottom flask (500 ml).

The progress of reaction was followed by estimating the residual hydrogen peroxide concentration left at different intervals of time iodometrically by taking out a liquor (2ml) with the help of a pipette.

In all the experiments it was ensured that the substrate i.e. NSSC pulp was always present in sufficient excess so that the rate of reaction with respect to hydrogen peroxide concentration, could be legitimately established by studying the changes occurred in the peroxide concentration, with time alone.

Progress of reaction between hydrogen peroxide and NSSC pulp was stopped after a specified time by adding

sodium metabisulphite solution to give pH of approximately 5 and oxidised pulp was then formed into handsheets.

Order of the reaction was determined by conducting a series of experiments at different initial hydrogen peroxide concentrations, $[H_2O_2]$, under otherwise constant conditions. The kinetic data were analysed by integration method by fitting the first order rate law equation i.e. $-dc/dt = kc$ or $k = 2.303/t \log_{10} a/a-x$, where a is the initial concentration of hydrogen peroxide and ' $a-x$ ' in the concentration at any time ' t '.

Preparation of Handsheets and Brightness Measurement :

The different pulps obtained after peroxide oxidation, conducted at various conditions, were formed into handsheet as per TAPPI standard T 218 m-59 method. The brightness of handsheets was measured by Elrepho photoelectric reflectance photometer.

RESULTS AND DISCUSSION

Pulp Analysis :

The pulp yield (o.d. basis), rejects, kappa number and klason lignin content in pulp were estimated as 78.8, 1.5, 95.9 and 12.7 percent respectively. Klason lignin content of depithed bagasse was also estimated and it was found to be 21.0 percent, which showed that during NSSC pulping 8.3 percent klason lignin was removed.

Order of the Reaction and Effect of Different Variables on the Reaction Rate

The values of logarithms of residual peroxide were plotted against time, and straight line correlations were obtained (Fig. 1). Alkaline peroxide oxidation of NSSC pulp followed a first order kinetics with respect to hydrogen peroxide concentration. After about 35-40 minutes, the reaction followed a different course with a decrease in the value of rate constant, although order was still the same i.e. first order.

The values of initial first order rate constant (K_1) were calculated from the initial slopes while the values of the subsequent slower first order rate constant (K_2) were calculated from the later slopes of the straight lines (Table—1).

Table-1 : Effect of variation of initial hydrogen peroxide concentration on rate constant and point increase in brightness of the NSSC pulp.

Conditions : Pulp consistency = 3%
 Temperature = 50°C
 pH = 11
 Time = 180 minutes

Initial H ₂ O ₂ Conc. × 10 ⁴ M : gpl	k ₁ × 10 ⁻⁴ Min. ⁻¹	k ₁ × 10 ⁴ Min. ⁻¹	Points increase in brightness Elrepho (MgO=100)
75	0.2550	47.98	18.94
100	0.3400	49.90	20.85
125	0.4250	52.58	22.65
150	0.5100	54.12	24.82

Table-2 : Effect of variation of temperature on rate constant and point increase in brightness of the NSSC pulp.

Conditions : Pulp consistency = 3%
 Initial H₂O₂ Conc. [H₂O₂]₀ = 125 × 10⁻⁴ M or 0.4250 gpl
 pH = 11
 Time = 180 minutes

Temperature °C	k ₁ × 10 ⁻⁴ Min. ⁻¹	Temp. Coeff.	Points increase in brightness Elrepho (MgO = 100)
30	23.80	—	3.0
40	37.22	1.56	5.6
50	52.58	1.41	7.3
60	85.21	1.62	7.0
Average Temp. Coeff.		1.53	

In the reaction of NSSC pulp with hydrogen peroxide the initial fast reaction is believed to be between peroxide and lignin whereas the later slowed reaction is believed to be between peroxide and lignin oxidation products and/or carbohydrate fraction etc. As peroxide-lignin reaction is mainly responsible for bleaching effect, only the kinetics data of the initial fast reaction have been discussed here.

The reaction rate was found to increase with the rise of the initial concentration of H₂O₂ applied (Table-1). A linear relationship was observed between the initial fast first order rate constant (k₁) and consistency

of the pulp under otherwise constant conditions (Fig.2). A perusal of the data in Table -2 showed that the initial fast first order rate constant (k₁) increases nearly one and a half times for every 10°C rise of temperature, the temperature coefficient being 1.53. When log k¹ values were plotted against 1/ T a straight line was obtained, Fig. 3, which showed alkaline peroxide oxidation of NSSC pulp followed Arrhenius equation. The reaction rate was found to be directly dependent on the pH or hydroxyl ion concentration (Table-3). Similar kinetic trends were observed by Vishnoi and Jain(1989) for alkaline peroxide oxidation of soda lignin isolated from depitched bagasse.

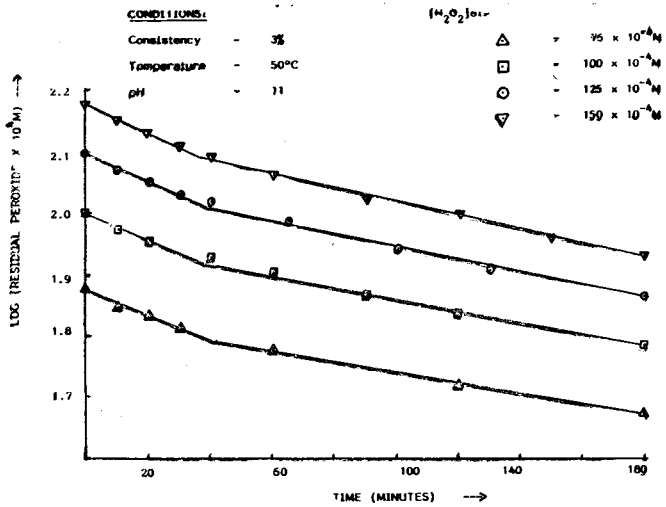


FIG.- 1 : ORDER OF THE REACTION WITH RESPECT TO PEROXIDE CONCENTRATION

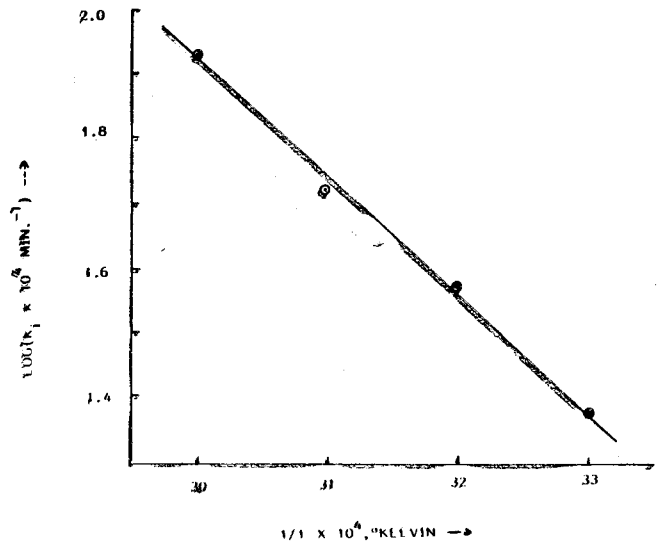


FIG.- 2 : ARRHENIUS PLOT FOR THE OXIDATION OF NSSC PULP

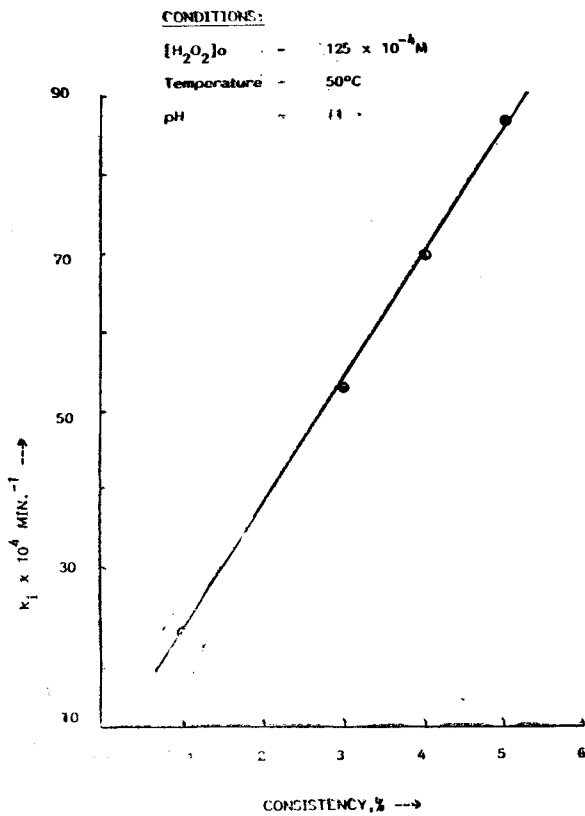


FIG.- 2 : RATE CONSTANT V/S CONSISTENCY

Table-3 : Effect of variation of pH on rate constant and point increase in brightness of the NSSC pulp.

Conditions : Initial H_2O_2 Con. $[H_2O_2]_0 = 125 \times 10^{-4} M$ or 0.250 gpl
 Pulp consistency = 3%
 Temperature = 50°C
 Time = 180 minutes

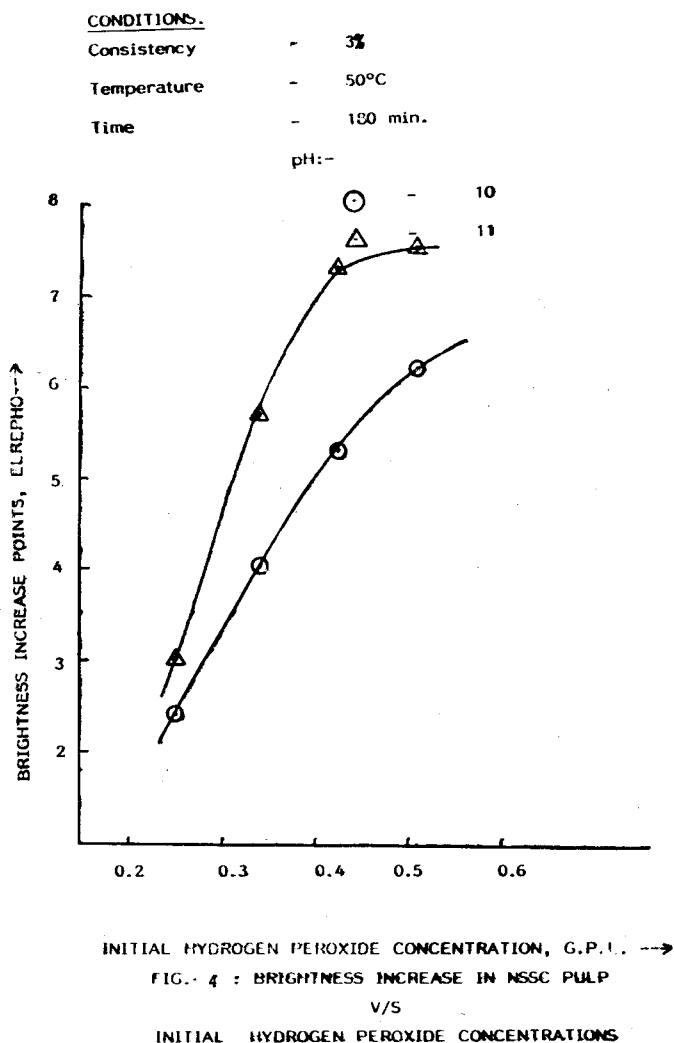
pH	k_1 $\times 10^{-4} \text{ Min}^{-1}$	Points increase in brightness Elrepho (MgO = 100)
9	31.47	3.0
10	41.07	6.2
11	52.58	7.3
12	79.45	6.6

Brightness Changes in Neutral Sulphite Semi Chemical Pulp :

While carrying out kinetic experiments it was observed that during storage for about 3 months of NSSC pulp there was fall in the brightness of the unbleached NSSC pulp from 41.2 to 39.0 Elrepho, with an average value of 40.1 Elrepho. This average value was taken as the brightness at zero time. Martin (1957) also considered this average brightness a reliable value.

Effect of initial hydrogen peroxide concentration on the brightness :

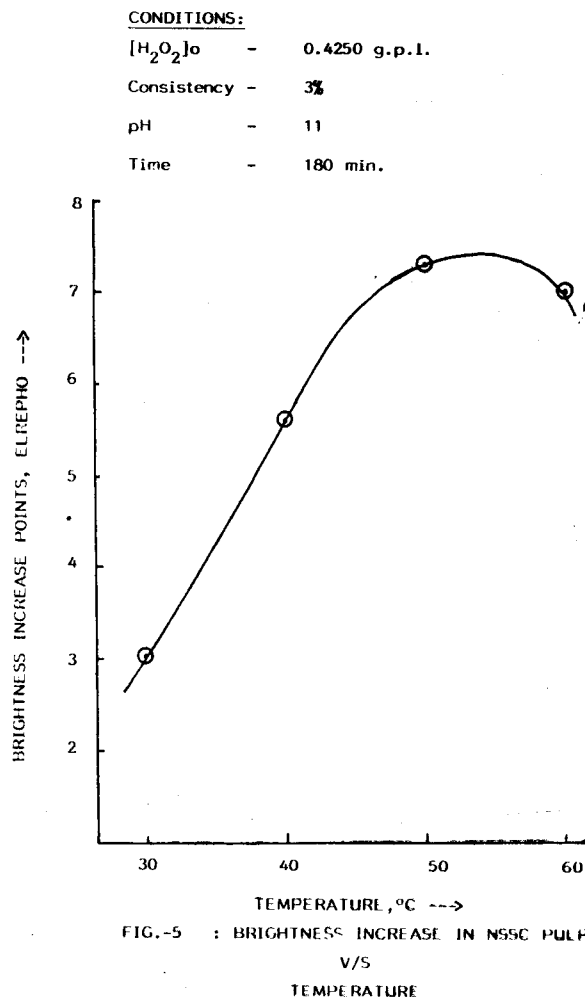
It was evident from the data (Table-1 and Fig. 4) that the brightness improvement of the bleached NSSC pulp handsheets increased with the increase in initial hydrogen peroxide concentration upto 0.51 gpl. But the rate



of increase in the brightness per unit of peroxide charge was levelled off with increase in initial hydrogen peroxide concentration. It was concluded that for economic consideration and brightness level requirement the concentration of hydrogen peroxide should not exceed 0.51 gpl. or 1.7 percent (o.d. basis of pulp).

Effect of temperature on the brightness :

Data represented in Table-2 and Fig. 5 showed that the increase in temperature from 30°C to 50°C had beneficial effect on brightness under specified conditions. But further increase in temperature decreased the brightness response i.e. brightness reversion took place. It may be concluded that the effect of increasing temperature on bleaching rate results in part from the equilibrium for hydrogen peroxide and water, $H_2O_2 + ^-OH \rightleftharpoons O^-OH + H_2O$, being shifted to the right increasing the concentration of the perhydroxyl anion (^-OOH), the active oxidizing species. This explanation was also



favoured by Kindron (1980). Increasing the temperature above 50°C not only enhanced the rate of bleaching but enhanced peroxide decomposition as well. It resulted in a net decrease of final brightness response. Further, at higher temperature, both heat and light induced brightness reversion possibly takes place (Joyce and Mackie 1979).

Effect of consistency on the brightness :

The results of the experiments conducted at different pulp consistencies have been represented in Fig 6. It is clear from the results that the consistency of the pulp during bleaching reaction had a marked effect on the brightness increase. Increased consistency, increases the bleaching response at constant peroxide to pulp ratio 1.42, 100). A straight line relationship was obtained between the brightness-increase and consistency at constant peroxide to pulp ratio. Higher consistencies (more than 9 percent) were not tried as the mixing was difficult.

Effect of pH and time on the brightness :

The brightness of the bleached NSSC pulps obtained from the experiments conducted for different period at different pH levels has been represented in Fig. 7. It was observed that brightness increase was more in the earlier stage of the reaction than the later stages at all the pH levels from 9 to 12. At pH 12 there was a fall in rate of brightness increase after a certain lapse of time. The maximum increase of brightness was substantial with the increase in pH from 10 to 12 and the time taken to achieve the maximum increase in brightness showed a decreasing trend with the increase in pH.

It may be said that for maximum brightness gain the total alkalinity of the bleach liquor should be high enough to ensure an adequate concentration of perhydroxyl anion, the active bleaching species as dictated by the equilibrium, $H_2O_2 + ^-OH \rightleftharpoons ^-OOH + H_2O$. At the same time, the alkalinity must be low enough to minimise peroxide decomposition and chromophore forming reactions that are prone to occur at high pH (pH 12). This has been substantiated by a number of researchers (Kindron 1978, Flowers and Banham. 1985, Moldenius and Sjogreu, 1982 and Moldenius 1984).

CONDITIONS:

$[H_2O_2]_0$	-	1.42% (o.d. basis)
Temperature	-	50°C
pH	-	11
Time	-	180 min.

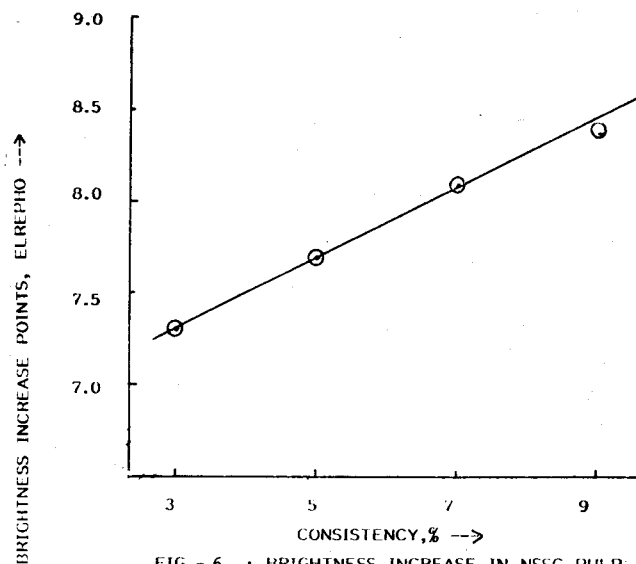


FIG.- 6 : BRIGHTNESS INCREASE IN NSSC PULP V/S CONSISTENCY

CONDITIONS:

$[H_2O_2]_0$	-	0.4250 g.p.l.	pH:-
Consistency	-	3%	▽ - 9
Temperature	-	50°C	□ - 10
			△ - 11
			○ - 12

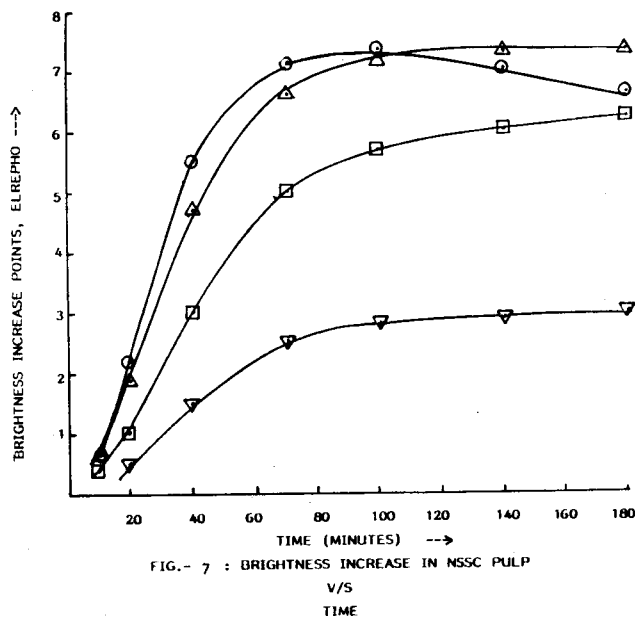


FIG.- 7 : BRIGHTNESS INCREASE IN NSSC PULP V/S TIME

Rate Constant as Controlling Factor for Obtaining Optimum Increase in the Brightness :

The brightness-increase w r.t. rate constants corresponding to different initial hydrogen peroxide concentration, temperature and pH levels has been recorded in Table 1, 2 and 3 and represented graphically in Fig. 8, 9 and 10 respectively.

It is obvious from Fig. 8 that at both the pH levels of 10 and 11, the brightness increase of pulp tends to level off when the value of k_i exceed $55 \times 10^{-4} \text{Min}^{-1}$. In Fig. 9 and 10 also the brightness increase of pulp is maximum when the value of k_i exceeded $55 \times 10^{-4} \text{min}^{-1}$ with the increase of temperature or pH whereas with the value of k_i exceeding $60 \times 10^{-4} \text{Min}^{-1}$, the brightness decreases. It was concluded from the above study that there is some short of optima in the value of rate constant ($k_i = 55 \times 10^{-4} \text{mine}^{-1}$), as far as the bleaching efficiency of NSSC pulp is concerned. It is clear that the value of rate constant between $55 \times 10^{-4} \text{Min}^{-1}$ to $60 \times 10^{-4} \text{Min}^{-1}$ yields the maximum brightness increase of NSSC pulp and hence the conditions of alkaline

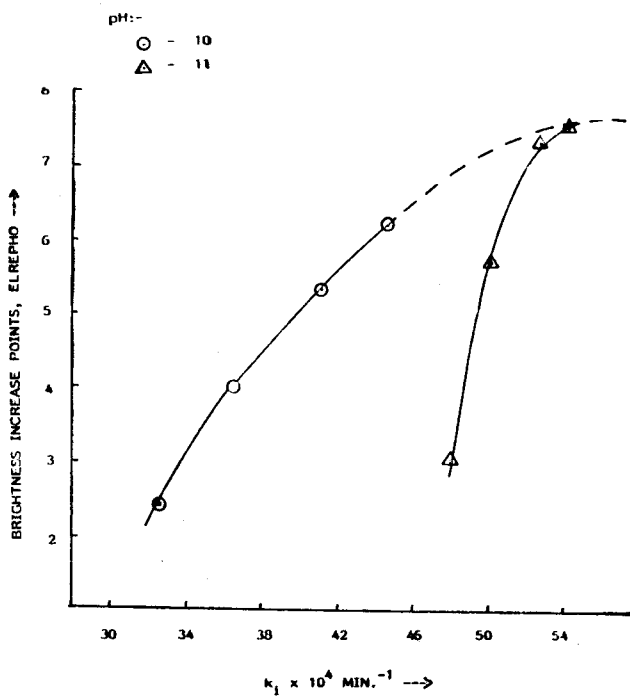


FIG. 8 : BRIGHTNESS INCREASE IN NSSC PULP V/S RATE CONSTANT AT DIFFERENT INITIAL PEROXIDE CONCENTRATIONS

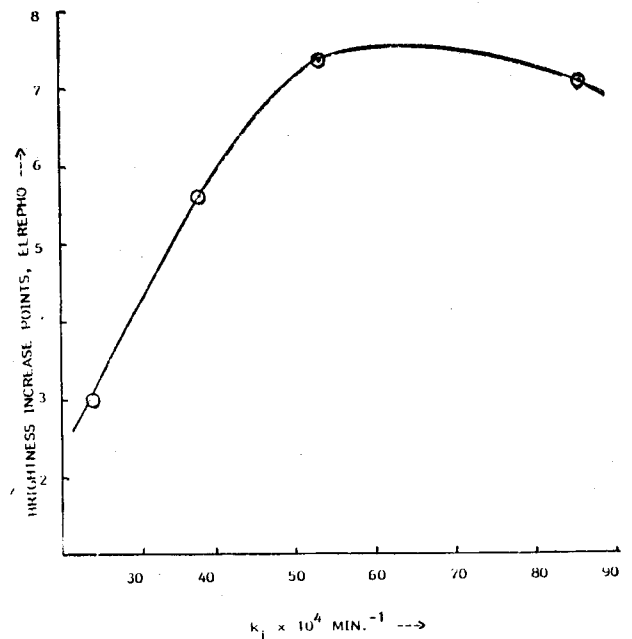


FIG. 9 : BRIGHTNESS INCREASES IN NSSC PULP V/S RATE CONSTANT AT DIFFERENT TEMPERATURES

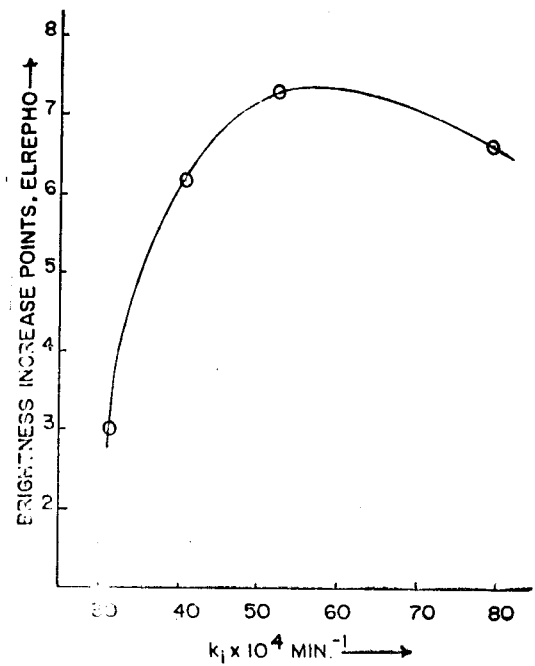


FIG. 10: BRIGHTNESS INCREASE IN NSSC PULP V/S RATE CONSTANT AT DIFFERENT pH LEVELS

peroxide oxidation (bleaching) should be adjusted in such a way so that the rate constant attains the value within the range as mentioned above.

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