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Bleaching of High Yield Mutual Sulphite Semichemical Pulp

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BLEACHING OF HIGH YIELD NEUTRAL SULPHITE SEMICHEMICAL PULP

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ABSTRACT

The objective of this research project was to investigate the effect of various bleaching agents and procedures on brightness, degree of yellowness and retention of the original high yield of the unbleached neutral sulphite semichemical pulp.

In order to avoid excessive losses in bleaching of the high yield pulp, it was decided to limit the selection of bleaching chemicals to hypochlorites, peroxides and hydrosulphites. Furthermore, caustic extraction was to be employed only under relatively mild conditions as to temperature and concentration.

Based on the experimental conditions and results described in this report and on the use of an unbleached pulp with relatively low brightness of 32 percent, the following conclusions were drawn:

Bleaching of neutral sulphite semichemical pulp by means of one stage calcium hypochlorite treatment brought about only limited brightness development with concurrent relatively high yellowness.

Two stage bleaching with calcium hypochlorite was found to be more effective than one stage bleaching for a given amount of chemical. Best results were obtained when about 25 percent of the total hypochlorite were used in the first stage and the remaining 75 percent in the second stage.

Caustic extraction between two stages of hypochlorite bleaching improved brightness and reduced the yellow cast

of the bleached pulp. With this procedure, best results were obtained by using 50 to 75 percent of the total hypochlorite in the first stage.

Pulp bleached with hypochlorite followed by acidification and hydrogen peroxide treatment produced encouraging results as to brightness and decrease yellow cast.

Zinc hydrosulphite, although it did not improve brightness was effective in reducing the yellow cast of the bleached pulp.

All experiments caused only modest shrinkage of the pulp used.

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SURVEY OF LITERATURE

Introduction

Bleaching, as intended in this investigation, is based on the elimination of coloring materials by oxidation, mild alkaline extraction after oxidation, reduction, or a combination of these reactions, and should meet the following requirements:

(a) to produce a bleached material of acceptable whiteness with a minimum of fiber degradation,

(b) to retain, as much as possible, the high yield of the unbleached pulp,

(c) to permit technically and economically feasible operation.

The literature survey which follows, includes the bleaching of the following high yield pulps: groundwood, hardwood semichemical and cold soda pulp. This broad literature investigation has the purpose to investigate, relate and apply in the bleaching of high yield hardwood neutral sulphite semichemical pulp the experiences which the investigators reported in their areas.

Definitions

Bleaching of pulp is a process of treating fibrous raw materials with one or several chemicals by means of which the dull color of the unbleached pulp is altered to white color or to high brightness.

Three general approaches to bleaching have been proposed by Hatch (1):

(1) The production of pulp of acceptable color and brightness whereby hardly any purification occurs and losses are kept to a minimum. This refers to groundwood and high yield unbleached pulps down to about 62 percent yield based on oven dry wood.

(2) The production of pulp of desirable color and brightness with moderate purification and losses. This includes pulp commonly known as bleached kraft, bleached sulphite, bleached soda, and bleached neutral hardwood semichemical with yields of about 62 percent to 40 percent based on oven dry wood.

(3) Purification of pulp to high alpha cellulose content and, as a secondary effect, to pulp of high brightness. This category comprises dissolving pulps and pulps used in papermaking under the name of alpha pulp.

The development of high yield unbleached pulp brought about an intensified interest in maintaining the initial quantity of the unbleached pulp throughout the bleaching operation, and in maintaining, whenever possible, the inherent strength characteristics of the fiber.

From the standpoint of bleaching as an operation to whiten the pulp, spectral reflectivity and specifically, brightness, are variables of importance.

Spectral reflectivity (2) can be expressed in a form of a curve giving reflectivity as a function of wavelength over the range of the visible spectrum, namely, 400 to 700 millimicrons. Reflectivity is the ratio of the amount of light reflected by the sample of pulp to that reflected from a pure and properly prepared surface of magnesium oxide.

Color of pulp (2) is specified according to the standard observer and colorimetric coordinates system, recommended in 1931 by the International Commision on Illumination.

The term brightness (3) as applied to white or near white papers has come to be associated with the numerical value of the reflectance of those papers to light in the blue and violet portions of the spectrum, the measurement being made by means of an instrument known to be in calibration with a master instrument of particular type and design.

Chemistry of Peroxide with Respect to Bleaching

Thenard is credited for the discovery of hydrogen peroxide while studying the action of acids on the oxides of metals.

The structure of hydrogen peroxide, as determined by the molecular weight and stoichiometry of its reactions has been found to correspond to H_2O_2.

Hydrogen peroxide is the simplest member of the peroxide family which is a class of compounds that contains directly bound oxygen atoms. The rather unstable peroxide configuration -O-O- has the inherent nature of presenting strong power of oxidation which decomposes easly to elemental oxygen.

There exist several reasonable configurations of the molecule H_2O_2 (4) but two general forms have been the basis of discussion: in one, each hydrogen atom is attached to a different oxygen atom having a catenate arrangement of the atoms; in the second form, both hydrogen atoms and one oxygen atom are attached about a central atom.

Hydrogen peroxide is a weak acid; sodium peroxide is its salt. In water solutions, hydrogen peroxide is slightly ionized according to the equation:

$$H_2O_2 + H_2O \rightleftharpoons H_3O^+ + HO_2^-$$

and the presence of hydroxyl ions promotes the dissociation whereby elemental oxygen is released.

Hydrogen peroxide is a bleaching agent and although considerable work has been done on its manufacture, properties, technology, and, uses, little is known on the nature of the chemical reactions by which peroxide decomposes colored materials.

In addition to the information given above, hydrogen peroxide decomposes according to the following equation:

$$H_2O_2 \rightleftharpoons H^+ + HO_2^-$$

and its bleaching action is attributed to the formation of the perhydroxyl radical (HO_2^-); furthermore, an increase in pH is followed by an increase in the rate of bleaching. It is agreed that the oxygen released by the decomposition of hydrogen peroxide has no bleaching effect. Scheller (5) found that there is a distinctive difference between the effects of elemental and active oxygen on cellulose in the presence of alkali, namely, that cellulose is not attacked by alkali in the absence of oxygen; on the other hand, the presence of elemental oxygen (air) is harmful. The magnitude of this degradation depends on the alkali concentration, temperature and surface exposed to the chemical. Active oxygen, in contrast, does not harm the fiber in the presence of alkali, particularly as long as the bleaching with active oxygen is carried out so that no rapid decomposition of peroxide with development of elemental oxygen occurs. In a correctly directed bleaching procedure, the radicals -O-O-H or -O-O-Na react with the cellulose with no harmful degradation.

As mentioned before, only a few studies are available on the mechanism of pulp bleaching with peroxides. Jones (6), investigated the effect of sodium peroxide on bleaching of Eastern spruce groundwood and disclosed that there are no pronounced chemical changes of the known components in terms of currently used methods of wood analysis. The total lignin is responsible for about 40 percent and holocellulose for about 60 percent of the total sodium peroxide consumed. Methylation of the extracted lignin reduced markedly the amount of peroxide consumed in reacting with the lignin, from which it was assumed that the primary attack of peroxide on lignin is through a portion of the carbonyl or possibly phenolic hydroxyl groups. The characteristics of the reaction between sodium peroxide and isolated native lignin indicated that lignin is composed of two or more fractions which are essentially the same in elementary composition and methoxyl content but which differ with respect to color, and reactivity toward sodium peroxide. It is suggested that the bleaching efficiency of sodium peroxide may be due to high reactivity and specificity of peroxide with the most highly colored lignin fractions.

Effect of Catalysts on Peroxide

The catalytic effect of some multivalent metal compounds such as copper, iron, manganese, cobalt, and, nickel on the rate of decomposition of peroxide solutions is of great importance in bleaching. This catalytic effect has the inherent tendency of a spontaneous evolution of oxygen. Holst (7) presumes that the tendency of producing perhydroxyl radicals (HO_2^-) and perhydroxyl ion (O_2^-) from hydrogen peroxide in solution at varying pH should be determined by the potential of the following half-reactions:

$$H_2O_2 \rightleftharpoons HO_2 + H^+ + e \qquad (pH < 8.5)$$

$$H_2O_2 + 2OH^- \rightleftharpoons O_2^- + 2H_2O + e \qquad (pH = 8.5 - 11.6)$$

$$HO_2^- + OH^- \rightleftharpoons O_2^- + H_2O + e \qquad (pH > 11.6)$$

Holst states further that in acid solution, the slow generation of HO_2^- radicals may be defined by the difference between potentials of the half-reactions:

$$2H_2O \rightleftharpoons H_2O_2 + 2H^+ + 2e \qquad (1.8\ e.v.)$$

$$H_2O_2 \rightleftharpoons HO_2 + H^+ + e \qquad (1.5\ e.v.)$$

while the great potential difference of the half-reactions:

$$H_2O_2 \rightleftharpoons HO_2 + H^+ + e \qquad (1.5\ e.v.)$$

$$HO_2 \rightleftharpoons O_2(g) + H^+ + e \qquad (-o.1\ e.v.)$$

should govern the subsequent evolution of oxygen.

The presence of minute quantities of heavy metals act as a powerful catalyst in this decomposition which appears to be greatly increased in the presence of alkali.

Holst suggests that the addition of various substances such as sodium silicate and sodium stannate which upon hydrolysis yield extremely fine colloidal dispersions of silisic and stannic acid, dilute or concentrated solutions of hydrogen peroxide may be stabilized.

Reichert (15), who made extensive studies on the subject, suggests the use of sodium silicate or magnesium sulphate stabilizers to deactivate metal catalysts.

Variables in the Bleaching of Groundwood with Peroxide

Effect of Temperature

Reichert (8), states that temperature has a definite effect not only on the rate of bleaching, but also on the resulting brightness. In a succeeding study, Reichert (9) considers the effects of a temperature range from 20 to 50 C and concludes that with an increase in temperature, a decrease in bleaching time is observed. Kauffmann (10), supports the hypothesis that the catalytic and oxidation reactions of peroxide increase with an increase in temperature. Stobo (13), carrying out bleaching of groundwood at temperatures varying between 11 and 55 C has obtained indications that neither increase nor final brightness are critically influenced by variation in temperature, that no significant gain is obtained below 40 C, and that at high temperatures, there are indications of a resulting decrease in brightness. However, Stobo states that temperature has a marked effect on the bleaching time with the best results obtainable between 40 and 50 C. Brecht (11), concludes from his studies that both the brightness as well as the bleaching time are dependent upon the temperature, and that the best results are obtained at about 40 C. Mc Ewan (12), who also has investigated the effect of temperature variation, has found that maximum brightness is obtained in the range of 40 to 60 C at consistencies of about 25 percent. Any further increase in temperature was found to result in a decrease in brightness.

In conclusion, the above mentioned investigators appear to agree that the maximum beneficial effect of temperature in bleaching of groundwood is obtained at about 40 C.

The Effect of Consistency

The consistency at which groundwood is bleached appears to be an important factor. Reichert (8), observed an increase in the brightness with an increase in consistency within the range of 3.0 to 7.0 percent. The bleaching time is also favourably affected by an increase in consistency. Kauffmann (10) also attributes to consistency a decided influence on the production of maximum brightness with a given amount of peroxide. Mc Ewan (12), has demonstrated from his work the significant advantage in operating at high consistency. In some cases, as much as 50 percent increase in brightness had been obtained at the same chemical consumption when bleaching at 25 percent rather than at 3.0 percent consistency. Another advantage of the effect of consistency was shown in the same study by Mc Ewan with groundwood from Southern pine and Western hemlock. The experimentations showed that low density operation result in little or no increase in brightness when using two percent hydrogen peroxide whereas, when the same pulp was bleached at 25 percent consistency, the bleach response was considerable. Stobo (13), agrees with the former experimentors as to the beneficial effect of an increase in consistency; however, he found that, up to 15 percent consistency, brightness improvements are noted and that higher values produce no further increase, and, in some cases, slight losses in brightness were observed. Furthermore, his experiments pointed out that brightness at 15 percent consistency were not consistently greater than at seven percent consistency. Stobo attributes the discrepancy between his results and the ones obtained from other investigators partly to the technique of bleaching. Brecht (11), experimenting over a range of 3.5 to 18 percent consistency has found that maximum brightness is obtained at eight percent consistency although the time of bleaching continued to decrease with increasing consistency. The achievement of a maximum has been explained in terms of the law of mass action and the decrease in the rate of diffusion.

In conclusion, all the above investigators observed an increase in brightness due to an increase in consistency; however, the consistency at which the maximum beneficial effects are obtained seem to vary with the species of wood and the technique of bleaching.

Effects of Quantity of Bleaching Agents and Time

The amount of bleaching agent to be used is of the utmost importance in the achievement of brightness and from the economical point of view.

Kauffmann (10), states that an increase in hydrogen peroxide concentration in the mixture to be bleached is followed by an increase in brightness, and that at lower concentrations of the peroxide, this increase in concentration is almost proportional to the increase in brightness. At higher concentrations, the increase in brightness becomes less. Brecht (11), working within a range of 0.5 to 5.0 percent peroxide based on oven dry pulp, found that two percent peroxide produced the best results and maximum brightness was obtained in a period of one to three hours. Stobo (13), points out that brightness continues to increase over a period of two to three hours, and therefore, develops the assumption that brightness increase occurs in two stages, the first, an extremely rapid reaction, followed by a slower reaction in which the brightness is further developed.

There seems to be an agreement that about two percent peroxide based on oven dry pulp appears to be a realistic figure for bleaching groundwood. Variations in the amount of peroxide may be attributed to such factors as type of wood, impurities in the wood and mill equipment, and age of wood or pulp.

Kauffmann (10), states that a greater brightness increase is obtained on spruce, balsam, and, poplar than on pine and Western Hemlock. Considerable resistance to peroxide bleaching is also present when logs are infested with certain fungus groth.

Effect of pH Level

The hydrogen ion concentration is another important variable in the bleaching of groundwood with peroxides.

Reichert (14), investigating the alkaline concentration in the bleaching of groundwood with sodium peroxide has found that sodium peroxide buffered with sodium silicate alone is too alkaline to produce good results and that at such high alkalinities, the pulp turns yellowish in color. Later studies carried out to determine the effect of silicate concentration showed that its concentration is not critical if maintained around five percent. Mc Ewan (12), states that six to eight percent silicate is found to be optimum percentage in the bleaching at low and high densisties. The variation of alkali was studied by Reichert and cowrokers (9) over a wide range, either by using sulphuric acid or sidum hydroxide on a constant amount of two percent sodium peroxide, five percent sodium silicate, at 32 C and at five percent consistency for six hours. Brightness was found to increase until a concentration of 0.75 percent caustic soda was reached. Further increments in caustic concentration resulted in rapid decrease in brightness. The experiments showed that the best formula for bleaching groundwood with two percent sodium peroxide and five percent sodium silicate will require for neutralization 1.7 percent sulphuric acid. Stobo (13), attempts to define optimum alkalinities conditions in terms of pH, rather than based on the amount of acid to be added to the bleaching solutions of definite make up. He found that the optimum pH varies with consistency - that at a consistency of seven percent, maximum brightness is obtained at pH 11.75, while at 15 percent consistency, the optimum pH dropped to 11.1 to 11.2.

In conclusion, it appears that for sodium peroxide bleaching the percentage of silicate is not critical if its concentration is maintained between five and eight percent at low or high consistencies. The influence of pH is quite critical and the optimum range is to be found between 11.0 and 12.0, depending on consistency of bleaching.

Bleaching of Groundwood with Hypochlorite

A favourable bleaching effect of hypochlorite on groundwood pulp appears to depend chiefly on slowing the rate of reaction during the first few moments, when, a large portion of chlorine is consumed by the pulp (16). This initial rate of reaction can be adjusted by using suitable conditions as:

(a) Consistency

(b) Temperature

(c) Alkalinity

Effect of Consistency

Studies by Kingsbury (16), showed that somewhat higher brightnesses can be expected when bleaching with hypochlorites in the lower rather than at high consistency range. The consistency of about six percent was found to be satisfactory for groundwood pulps from sweetgum, post oak, water tupelo but not for those from yellow poplar and southern yellow pine.

Effect of Temperature

In bleaching groundwood pulp Kingsbury (16), found no advantages in using temperatures greater than 35 C. With some pulps, Kingsbury found that a temperature as low as 20 C may be necessary to slow the reaction sufficiently in order to obtain an increase in brightness as was the case for western hemlock.

Effect of Alkalinity

Kingsbury (16), found strong indications from his experiments that the initial pH of about eleven is required to obtain the maximum effect in brightness increase. The final pH is also important; there are indications that it should be on the alkaline side.

The beneficial effect of using sodium silicate in the bleaching of chemical pulps with hypochlorite reported by Carter (17) was also investigated by Kingsbury (16), and encouraging results were obtained in the form of brightness increase and decrease in yellowness. This suggests that sodium silicate has possibly the effect of a dispersant increasing the removal of colored reactive products during washing. It appears that the most effective concentration of sodium silicate has to be determined "in loco" although, two to ten percent may be considered as limits.

Brightness and Yellowness

Kingsbury (16), bleached a variety of groundwood pulps from hardwoods and softwoods with ten percent chlorine as hypochlorite and two percent sodium peroxide respectively. It was found that:

(a) Hardwood pulps respond well to hypochlorite and also with some exception, to sodium peroxide.

(b) The softwood pulps responded better to sodium peroxide than to hypochlorite. The effect of both bleaching agents was less in the case of softwood than for hardwood pulps.

(c) Brightness of groundwood pulps bleached with hypochlorite are less stable than when bleached with sodium peroxide.

With respect to yellowness, Kingsbury (16) found that bleaching with hypochlorite develops more yellowness than with sodium peroxide.

In a following study of the effects of bleaching groundwood pulp with hypochlorite, Kingsbury (18) found that the brightness of hardwood pulps could be increased in the range of 70 to 79 percent with ten percent available chlorine. This was accomplished by reducing the rate of reaction by the use of low densities, low temperature and high alkalinity, the latter being the most critical. The lime requirement for the control of alkalinity ranged between three and six percent including free lime in the bleaching liquor. Partial substitution of free lime by sodium silicate further improved brightness.

Bleaching of Groundwood Pulp with Hydrosulphites

Sodium hydrosulphite, zinc hydrosulphite and their corresponding sulphoxylate aldehyde derivatives are powerful reducing agents. This characteristic as well as the superior stability of the aldehyde addition products with respect to heat and oxidation by air (19) has been taken to great advantage in the textile industry in connection with some dyes for stripping colors from rags for re-use.

Variables in the Bleaching of Groundwood Pulp with Hydrosulphites

The bleaching of groundwood pulp with zinc hydrosulphite (ZnS_2O_4) is a Pacific Coast development due to the fact that bleaching of groundwood from western hemlock and balsam fir has a reddish color.

The commercial process of bleaching with zinc hydrosulphite, as described by Andrews (20), is based on the following experiences:

> At normal temperature of 20 to 27 C hydrosulphites produce brightening effects but considerable time

is required before maximum results are obtained. At elevated temperatures with hydrosulphite giving an alkaline reaction, as in case of sodium hydrosulphite, grayness develops, but zinc hydrosulphite yields higher brightness with an increase in temperature up to 93 C. Consistency of one to six percent do not appear to have any effect on brightness development.

For the manufacture of groundwood pulp for newsprint, the following requirements are suggested (20):

Zinc hydrosulphite	0.6 %
Temperature	66-60 C
Time	0:20 Hr.

and for groundwood of high brightness:

Zinc hydrosulphite	3 - 4 %
Temperature	71-74 C
Time	1:30-2:00 Hr.

Upon the corrosive nature of zinc hydrosulphite, Andrews (20), states that at normal bleaching consistencies of 2.5 percent up, no harmful corrosion occurs, but that upon dilution, the corrosiveness increases considerably. Cast iron and high chromium steel resist this corrosive action.

Barnes (21), investigated the influence of reaction temperature, reaction time, pH control and stock consistencies when bleaching western hemlock groundwood pulp with zinc hydrosulphite, and found that:

(a) The temperature of reaction is critical and establishes the brightness level in the first 20 minutes period where the bulk of bleaching occurs.

(b) Brightness levels obtained at high temperature and short retention time cannot be expected from long treatments at low temperature because zinc hydrosulphite decomposition and other secondary reactions.

(c) Loss in brightness may occur if treatments at high temperatures are too long.

(d) Brightness increases in increments of 0.4 to 0.5 units for each 7 C rise in temperature from 27 to 58 C.

(e) For efficient bleaching, 45 minutes retention is required at 58 C, and 60 minutes at 49 C. Similar increase in retention can be expected at lower temperatures.

(f) An additional increase in brightness is obtained by pH control. The most favourable pH values are: 3.5 for bleaching, 2.5 for washing and 4.5 to 5.5 for sheet making.

(g) High consistencies (three percent plus) are required for efficient bleaching.

Sparrow (22), studied the effect of the use of metal deactivators such as sodium salts of condensed polyphosphates or ehtylene-diamine-tetra-acetic acid (EDTA) in hydrosulphite bleaching of groundwood pulp mixture of spruce-balsam-jack pine, and concluded that such deactivators make possible a higher response to bleaching.

Yankowski (23), summarizes the bleaching methods of groundwood pulp in the following table:

	Peroxide	Hypochlorite	Hydrosulphite
Bleaching Chemicals	Na_2O_2, H_2SO_4, sodium silicate, epsom salt.	Calcium hypochlorite and caustic soda.	Zinc or sodium hydrosulphite
Percent Chemicals	Good gains up to three percent.	Good gains up to 15 percent.	Good gains up to one percent.
Pre-treatment	Calcium chlorite in many cases increases brightness 1-2 points.	None.	Na-tripolyphosphate in many cases increases 1-2 points in brightness.
Effect of Consistency	Increasing consistency: decreas. reaction time, increas. bright. gain.	Increasing conc.: reduces react. time, bleach. harder to control, best conc. 4-6%.	1-6% has no effect on bleach. Higher conc. yield poorer results due to mixing problems.
Effect of Temperature	Increasing temp.: decreas. reaction time, temperature range 30 to 70 C.	Increasing temp.: decreas. react. time, increas. bright.gain, bleach hard to control optimum temp. 38 C.	Increasing temp.: decreas. react. time, increas. bright.gain, temperature range 30 to 70 C.
pH and Alkalinity	pH range 10 to 10.5: poor results above or below this range.	pH range 9 to 11: pH 9 most effective but hard to control, pH 9.5-10.5 easy to control, pH below 9 or above 11 increas. chlorine consumption.	pH range 5 to 6.5: pH above 6.5 discolors pulp, pH below 4.5 aids in decomposition of liquor.
Further Treatment	Neutralization and acidification with SO_2.	Acidification with SO_2 and washing.	None.
Brightness gains	6-7 points for most woods with 1% chemical, 10-12 points for most woods with 2% chemical.	10%Cl_2: 12 points for hardwood. 15%Cl_2: 10 points for softwood.	1% chemical: 8-10 points for most woods.

Bleaching of Neutral Sulphite Semichemical Pulp with Hypochlorite

The bleaching of semichemical pulp with hypochlorite is, in many ways, analogous with the bleaching of groundwood pulp with hypochlorite. For instance, if hypochlorite is added to semichemical pulp with no extra alkalinity beyond lime saturation of the bleach liquor, a very rapid exhaustion of the bleach liquor occurs with very little brightening of the pulp. This unsatisfactory brightness development is attributed by Simmonds (24), as being possibly caused by a loss in potential oxidizing power of the available chlorine owing to the chlorination of lignin by hypochlorous acid and an attendant darkening of the pulp by the insoluble fraction of the chlorinated lignin.

Good judgment of consistency, temperature and alkalinity appears to be an important role for the obtention of high brightness. Parsons and Lausman (25), has investigated the effect of varying alkalinity ranges on aspen semichemical pulp and found that an increase in alkalinity is followed by an increase in bleaching time, increase in brightness and reduction of pulp strength.

In the case of calcium hypochlorite, Parsons and Lausman (25), have found that the highest brightness is obtained at a respective initial and final pH of 11.7 to 9.9 and for sodium hypochlorite at a pH of 11.7 to a final one of 8.9. Further increase in alkalinity showed no definite trend of brightness improvement.

Simmonds (26), also emphasizes the importance of high alkalinty and suggests that the initial pH of the bleaching mixture should be in the range of 10.5 to 11.0. Simmonds continues then by pointing out that the most effective results are obtained by establishing the optimum amount of alkali for each type of pulp.

Haywood (27), has studied the effect of single stage hypochlorite bleaching of canadian poplar and found that a portion of the lignin fraction was removed by the hypochlorite and that the brightness developed is not satisfactory.

Bleaching of Neutral Sulphite Semichemical Pulp with Peroxide

The use of peroxide in the bleaching of semichemical pulp is based mostly on the fact that peroxides whiten the pulp considerably with almost no loss in yield.

Kingsbury (28), made an exstensive study on the bleaching conditions of aspen semichemical pulp and found that the alkalinity as expressed in percent sodium oxide (based on the weight of the pulp) when using sodium peroxide should be of 20 to 36 percent. The consistency of the pulp should be, for best results, in the range of 12 to 15 percent. Temperatures of no less than 52 C are required to develop maximum brightness.

In a following study, Simmonds (29), investigated the performance of sodium peroxide and hypochlorite in one-stage bleaching of several hardwoods and found that peroxide like hypochlorite was not equally effective on all pulps. In general, ten percent chlorine as hypochlorite at a sufficiently high alkalinity gave a somewhat higher brightness than two to three percent peroxide.

With regards to hue, Simmonds (29), found that pulps bleached with hypochlorite showed definitely greater yellowness than those bleached with peroxide.

Simmonds (29), stated further that in bleaching with sodium peroxide a yield of about 96 to 99 percent is to be expected, while with hypochlorite the yield ranged from about 92 to 99 percent, that one to five percent of the total lignin content of the unbleached pulp was removed with sodium peroxide bleach and 18 to 40 percent in the case of hypochlorite.

Bleaching of Cold Soda to Medium Brightness

Bleaching experiments carried out by Nolan (30), on cold soda hardwood showed that it was impractical to bleach cold soda with peroxide alone. Furthermore, pre-acidification of the pulp with hydrochloric acid indicated that a slight gain in brightness is possible. The use of caustic extraction stage preceeded by hypochlorite and followed by hydrogen peroxide was found to be quite beneficial in the resulting brightness of the pulp. The yield of this treated pulp was of the magnitude of 90 to 93 percent.

Le Roy Bauer (31), found that cold soda produced by the Bauerite process can be bleached to 70-78 percent brightness by the use of acidification, three to four percent hydrogen peroxide (50%) and with a final stage of one percent sodium hydrosulphite treatment.

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Bleaching of High Yield Neutral Sulphite Semichemical Pulp

OBJECTIVE

The objective of this research project was to investigate the effect of various bleaching agents and procedures on brightness, degree of yellowness and retention of the original high yield of the unbleached neutral sulphite semichemical pulp.

EXPERIMENTAL DESIGN

In order to avoid excessive losses in bleaching of the high yield pulp, it was decided to limit the selection of bleaching chemicals to hypochlorites, peroxides and hydrosulphites. Furthermore, caustic extraction was to be employed only under relatively mild conditions as to temperature and concentration.

Several series of experiments were planned. After single stage bleaching with calcium hypochlorite over a range from 2.5 to 17.5 percent active chlorine, the effect of splitting the bleaching agent was to be explored. These two stage bleaching experiments were to be followed by three stage bleaching, using first hypochlorite thereafter caustic extraction and finally hypochlorite again. The design of these three series of experiments may be seen from Table I.

Table II shows the experimental design for bleaching with peroxide and hydrosulphite. These experiments were either to be carried out with unbleached pulp or with pulp partially bleached with hypochlorite. The effect of acidification of pulp before peroxide treatment was to be explored.

EXPERIMENTAL PART

Characteristics of the Unbleached Pulp

The pulp used throughout the experiments consisted of an unbleached neutral sulphite semichemical aspen pulp produced for the manufacture of corrugating medium. The unbleached pulp, was obtained from the fourth stage of a series of press washers after one pass through a Sprout Waldron refiner.

To obtain clean pulp, the coarse pulp was subjected to further refining, screening and Bauer centricleaning in pilot equipment before bleaching. This eliminated considerable amounts of shives and fiber bundles.

The Roe chlorine number of the pulp as received after refining, screening and centricleaning was determined according to TAPPI Standard T 202 m-45. The Roe values obtained were 16.0 percent for the pulp as received and 16.2 percent for the cleaned pulp. The slight difference between the two values could be explained by the slower rate of diffusion of chlorine gas in the pulp sample containing shives.

The brightness of the unbleached pulp, as measured by the IPC brightness tester was 32.0 percent.

Procedure for Bleaching Experiments

The following techniques were used in all bleaching experiments:

Bleaching with Hypochlorite: All experiments were run in duplicate using polyethylene bags containing twenty grams oven dry fiber. The quantities of chemicals used were based on oven dry unbleached fibers. Mixing of chemicals and pulp was accomplished by intermittent kneading of the bags which were immersed in a thermostatically controlled water bath adjusted to 25 C (77 F). Close pH control was kept throughout the bleaching period by addition of measured quantities of ten percent sodium hydroxide solution, care being taken not to bleach at a pH level lower than 9.4.

All bleaching experiments were ended when the titratable amount of chlorine in the pulp suspension was 0.2 percent plus or minus 0.05 percent.

Caustic Extraction: Caustic extraction was also carried out in polyethylene bags at ten percent consistency. The amount of sodium hydroxide based on oven dry unbleached pulp was varied from one to two to three percent. The temperature was held at 60 C (140 F) for a period of one hour.

Acidification of Pulp: The acidification step lasted for 15 minutes and was carried out with two percent sulphuric acid to a pH of 2.5 to 3. The consistency was of 4.5 percent. Glass beakers were used and the temperature was maintained at 25 C (77 F).

Bleaching with Hydrogen Peroxide: All bleaching experiments with hydrogen peroxide were carried out in polyethylene bags with the following quantities of chemicals added in the order listed:

(a) Distilled water at 90 C (194 F), sufficient to give ten percent consistency.

(b) 0.05 percent magnesium sulphate

(c) Five percent sodium silicate

(d) 2.6 percent hydrogen peroxide (50%)

All chemical quantities were based on oven dry weight of unbleached fibers. Sodium silicate was of the BW grade furnished by the

Philadelphia Quartz Company.

The initial bleaching pH level was from 10.7 to 11.2 and the final pH value 9.8. Sodium hydroxide solution was used to maintain the pH level at or above 9.8.

All experiments with peroxide were performed at ten percent consistency at 82 C (180 F) for 90 minutes.

Zinc Hydrosulphite Bleaching: All bleachings were carried out in open beakers with one percent zinc hydrosulphite based on oven dry unbleached pulp. The consistency was 4.5 percent. The temperature was kept at 63 C (145 F) and the pH level maintained between 5.0 and 5.5 by the addition of dilute sulphuric acid. The bleaching time was of one hour.

Washing of Bleached Pulp: All partially or fully bleached pulp samples were washed, after each stage, with distilled water and filtered on filter paper on a Buechner funnel. For calcium hypochlorite bleachings, washing was ended when the filtrate was clear and did not react with starch-iodide indicator paper.

For caustic extracted pulp, the washing was ended when the filtrate was clear.

All the remaining experiments were washed with six liters of distilled water using filter paper on a Bueachner funnel.

Forming of Handsheets for Optical Tests: A portion of the bleached pulp corresponding to five grams oven dry fiber was withdrawn, diluted to two liters with distilled water and cleared in a TAPPI disintegrator for five minutes. Two brightness sheets were foermed on a Bueachner funnel, pressed and dried according to TAPPI Standard T 218 m-48.

Yield Determination: The bleached and washed pulp was carefully separated from the filter paper and dried in an oven at 103 C to constant weight.

Determination of Brightness: Brightness values of all sheets were measured at an average effective wavelength of 457 millimicrons by means of the Institute of Paper Chemistry Brightness Tester. The TAPPI Standard method used was T 217 m-48.

Determination of Yellowness: Yellowness values were measured at an average effective wavelength of 606 millimicrons using number seven filter of the IP brightness tester.

Presentation of the Results

The resuts of the effect of single stage and two stage calcium hypochlorite bleaching with varying quantities of chlorine are tabulated in Table III and presented in the form of bar graphs in Fig. 1, Fig. 2, and, Fig. 3. Table III also shows the results of two stage calcium hypochlorite bleaching with an intermediate stage of mild caustic extraction. These results are also offered graphically in Fig. 4.

The results of the bleaching experiments carried out with peroxide and/or zinc hydrosulphite are found in Table IV. In graphical form, Fig. 5 shows the individual and combined effects of hydrogen peroxide as well as zinc hydrosulphite on unbleached pulp with and without acid treatment. Fig. 6 shows the effects of hydrogen peroxide and zinc hydrosulphite on pulp previously bleached with ten percent chlorine as hypochlorite. Fig. 7 presents the effects of hydrogen peroxide and zinc hydrosulphite on pulp bleached in a single stage with 15 percent chlorine and in two hypochlorite stages of 7.5 percent chlorine in each stage.

Discussion of Results

Single Stage Bleaching with Calcium Hypochlorite: Single stage bleaching with progressively increasing amounts of chlorine as hypochlorite indicated that rapid brightness development occured with the use of up to ten percent chlorine. Further amounts of chlorine brought about brightness increases at a lower rate. The brightness reached by using ten percent chlorine was 54.3 percent. All pulps bleached in a single stage were markedly yellow. Additional amounts of chlorine did not decrease this yellow cast.

The yield of the single stage bleached pulps was satisfactory, i.e. never lower than 98.0 percent based on oven dry unbleached pulp.

Two Stage Bleaching with Calcium Hypochlorite: Two stage bleaching gave higher brightness than single stage bleaching for comparative amounts of chlorine. This increase in brightness, due to splitting of the total chlorine used, was in the order of magnitude of four percent.

When bleaching with ten percent total chlorine as hypochlorite, the best results on brightness, yellowness and yield were obtained by using 25 percent of the total chlorine in the first stage. Single stage bleaching with ten percent chlorine produced brightness of 54.3 percent, while bleaching in two stages with a 25-75 split yielded a brightness of 58.5 percent.

Bleaching with 12.5 percent chlorine as hypochlorite showed that best results could be obtained by using 40 percent of the total chlorine used in the first stage and the remaining 60 percent in the second stage. In this instance, an increase of 4.8 percent in brightness could be observed over comparative single stage bleaching. The yellowness also increased by 2.8 percent.

The bleaching experiments carried out with 15 percent chlorine as hypochlorite indicate that the 50-50 split yields the highest brightness as observed from bleaching experiments number 30, 29 and 26 in Fig. 2.

The yields obtained by bleaching with comparative amounts of chlorine as hypochlorite were practically identical in the cases of single and two stage procedures.

Mild Caustic Extraction Between Two Stage Calcium Hypochlorite:

Caustic extraction was found to be beneficial. It improved brightness and reduced yellowness.

Best results were obtained with two and three percent caustic soda. In general, two percent was found to be preferable because the effects obtained by higher concentration of caustic soda did not yield sufficient return.

To obtain maximum benefits from caustic extraction, the quantity of hypochlorite used in the first stage had to be larger than the quantity used in the final stage.

Bleaching of Unbleached Pulp with Hydrogen Peroxide and Zinc Hydrosulphite:

The direct application of hydrogen peroxide to unbleached pulp was found to be limited in usefulness. The brightness obtained in this experiment was merely 47.1 percent.

Likewise, zinc hydrosulphite did not show any promises as bleaching agent, neither when used alone nor when used after peroxide bleaching of the unbleached pulp.

Pre-acidification of the unbleached pulp prior to any of the three above experiments did not improve the performance of the bleaching agents.

Effect of Peroxide and Zinc Hydrosulphite on Hypochlorite Bleached Pulp:
Peroxide and hydrosulphite became far more useful as bleaching agents for pulp partially bleached with hypichlorite.

Pulp bleached with ten percent chlorine as hypochlorite, followed by 2.6 percent hydrogen peroxide, reached a brightness of 63.6 percent (experiment 39). If one compares this brightness value with the one obtained in experiment 26, namely 64.1 percent, it becomes evident that, in terms of brightness, treatment with ten percent chlorine followed by 2.6 percent hydrogen peroxide is as effective as treatment with hypochlorite in two stages using in each 7.5 percent or a total of 15 percent chlorine.

Pre-acidification was effective as intermediate step between treatment with ten percent chlorine as hypochlorite and bleaching with 2.6 percent hydrogen peroxide. In this instance, 5.3 percent brightness increase could be observed and the pulp reached a brightness of 68.9 percent.

Additional treatment with zinc hydrosulphite to the pulp reduced the brightness slightly to 66.2 percent but was quite effective in diminishing the yellow cast of the pulp from 83.2 to 80.5 percent.

In this series of experiments, the results of yield determinations were from 93.5 to 98.0 percent based on unbleached pulp.

Higher brightness values in the range from 69.1 to 73.6 percent with corresponding yellowness from 80.4 to 83.1 percent were obtained, by increasing the quantity of chlorine used as hypochlorite to 15 percent without any change in pre-acidification, peroxide and, when using hydrosulphite treatment. Best results were obtained when the hypochlorite was added to the pulp in two equal portions. Yield figures were in the satisfactory range of 93.0 to 94.6 percent.

CONCLUSION

Based on the experimental conditions and results described in this report and on the use of an unbleached pulp with relatively low brightness of 32 percent, the following conclusions may be drawn:

Bleaching of neutral sulphite semichemical pulp by means of one stage calcium hypochlorite treatment brought about only limited brightness development with concurrent relatively high yellowness.

Two stage bleaching with calcium hypochlorite was found to be more effective than one stage bleaching for a given amount of chemical. Best results were obtained when about 25 percent of the total hypochlorite were used in the first stage and the remaining 75 percent in the second stage.

Caustic extraction between the two stages of hypochlorite bleaching improved brightness and reduced the yellow cast of the bleached pulp. With this procedure, best results were obtained by using 50 to 75 percent of the total hypochlorite in the first stage.

Pulp bleached with hypochlorite followed by acidification and hydrogen peroxide treatment produced encouraging results as to brightness and decrease yellow cast.

Zinc hydrosulphite, although it did not improve brightness was effective in reducing the yellow cast of the bleached pulp.

All experiments caused only modest shrinkage of the pulp used.

Teodoro E. Reinhardt

Kalamazoo, Michigan
June 13, 1958

Table I

EXPERIMENTAL DESIGN

Calcium Hypochlorite Bleaching

With and Without Mild Caustic Extraction

Identification		First Step Calcium Hypochlorite Chlorine Percent		Second Step Caustic Extraction Sodium Hydroxide Percent		Third Step Calcium Hypochlorite Chlorine Percent
1		2.5		- -		- -
2		5.0		- -		- -
3		7.5		- -		- -
4		10.0		- -		- -
5		7.5		- -		2.5
6		7.5		1.0		2.5
7		7.5		2.0		2.5
8		7.5		3.0		2.5
9		5.0		- -		5.0
10		5.0		1.0		5.0
11		5.0		2.0		5.0
12		5.0		3.0		5.0
13		3.8		- -		6.2
14		2.5		- -		7.5
15		2.5		1.0		7.5
16		2.5		2.0		7.5
17		2.5		3.0		7.5
18		1.3		- -		8.7
19		12.5		- -		- -
20		7.5		- -		5.0
21		5.0		- -		7.5
22		5.0		2.0		7.5
23		5.0		3.0		7.5
24		2.5		- -		10.0
25		15.0		- -		- -
26		7.5		- -		7.5
27		7.5		2.0		7.5
28		7.5		3.0		7.5
29		5.0		- -		10.0
30		2.5		- -		12.5
31		17.5		- -		- -
32		7.5		3.0		10.0

Notes: (1) All percentages are based on oven dry unbleached pulp.
(2) Each step (treatment) was followed by washing with distilled water.

EXPERIMENTAL DESIGN

Combination of Various

Bleaching Agents

Identification	Calcium Hypochlorite Chlorine Percent	Acidification	Hydrogen Peroxide Percent	Zinc Hydrosulphite Percent
33	- -	- -	2.6	- -
34	- -	- -	- -	1.0
35	- -	- -	2.6	1.0
36	- -	yes	2.6	- -
37	- -	yes	- -	1.0
38	- -	yes	2.6	1.0
39	10.0	- -	2.6	- -
40	10.0	- -	- -	1.0
41	10.0	- -	2.6	1.0
42	10.0	yes	2.6	- -
43	10.0	yes	- -	1.0
44	10.0	yes	2.6	1.0
45	15.0	yes	2.6	- -
46	15.0	yes	2.6	1.0
47	7.5 + 7.5	yes	2.6	- -
48	7.5 + 7.5	yes	2.6	1.0

Notes: (1) All percentages are based on oven dry unbleached pulp.
(2) Each treatment was followed by washing with distilled water.
(3) Acidification was performed by the use of dilute sulfuric acid.
(4) 50% hydrogen peroxide was used and based on oven dry pulp.

SUMMARY OF RESULTS

The Effect of Single and Two Stage Bleaching

With Varying Quantities of Hypochlorite

Identification	Calcium Hypochlorite		Caustic Extraction		Calcium Hypochlorite		Total Chlorine Used	Total Sodium Hydrox. Used	Total Bleaching Time	Final Brightness	Final Yellowness	Final Yield
	Chlorine Used Percent	Bleaching Time hr	Sodium Hydrox. Used Percent	Time hr	Chlorine Used Percent	Bleaching Time hr	Percent	Percent	hr	Percent	Percent	Percent
1	2.5	0:11	- -	- -	- -	- -	2.5	0.5	0:11	31.2	55.3	99.3
2	5.0	0:39	- -	- -	- -	- -	5.0	0.8	0:39	37.5	65.3	99.2
3	7.5	1:15	- -	- -	- -	- -	7.5	1.5	1:15	46.5	73.5	99.0
4	10.0	2:25	- -	-	- -	- -	10.0	1.5	2:25	54.3	78.7	98.5
5	7.5	1:18	- -	- -	2.5	1:40	10.0	1.7	2:58	56.9	81.1	98.0
9	5.0	0:30	- -	- -	5.0	3:50	10.0	2.0	4:20	57.7	80.2	96.8
13	3.8	0:21	- -	- -	6.2	3:00	10.0	2.5	3:21	57.5	79.5	99.0
14	2.5	0:12	- -	- -	7.5	3:45	10.0	2.0	3:57	58.5	79.9	98.5
18	1.3	0:08	- -	- -	8.7	1:40	10.0	2.1	1:48	54.0	77.8	99.0
19	12.5	2:50	- -	- -	- -	- -	12.5	2.3	2:50	56.2	79.8	98.5
20	7.5	1:15	- -	- -	5.0	9:01	12.5	2.5	10:16	61.0	82.2	98.6
21	5.0	0:36	- -	- -	7.5	6:46	12.5	2.5	7:22	61.4	83.0	98.4
24	2.5	0:12	- -	- -	10.0	4:36	12.5	2.3	4:48	55.0	78.8	98.1
25	15.0	3:28	- -	- -	- -	- -	15.0	3.1	3:28	59.4	81.0	98.0
26	7.5	1:26	- -	- -	7.5	8:01	15.0	3.0	9:27	64.1	83.4	98.1
29	5.0	0:41	- -	- -	10.0	7:03	15.0	3.3	7:44	63.6	83.2	97.9
30	2.5	0:13	- -	- -	12.5	5:06	15.0	3.0	5:19	61.3	82.3	97.9
31	17.5	4:10	- -	- -	- -	- -	17.5	3.5	4:10	61.3	82.1	98.7

Caustic Extraction

Effect on Bleaching with Calcium Hypochlorite

Identification	Chlorine Used Percent	Bleaching Time hr	Sodium Hydrox. Used Percent	Time hr	Chlorine Used Percent	Bleaching Time hr	Total Chlorine Used Percent	Total Sodium Hydrox. Used Percent	Total Bleaching Time hr	Final Brightness Percent	Final Yellowness Percent	Final Yield Percent
5	7.5	1:18	- -	- -	2.5	1:40	10.0	1.7	2:58	56.9	81.1	98.0
6	7.5	1:10	1.0	1:00	2.5	4:00	10.0	3.3	6:10	57.7	81.2	96.8
7	7.5	1:22	2.0	1:00	2.5	4:30	10.0	4.0	6:52	61.4	82.1	96.0
8	7.5	1:27	3.0	1:00	2.5	5:40	10.0	5.0	8:07	61.1	81.8	93.5
9	5.0	0:30	- -	- -	5.0	3:50	10.0	2.0	4:20	57.7	80.2	96.8
10	5.0	0:28	1.0	1:00	5.0	4:50	10.0	3.0	6:18	59.5	81.3	97.5
11	5.0	0:31	2.0	1:00	5.0	5:05	10.0	4.0	6:36	60.3	81.7	95.5
12	5.0	0:30	3.0	1:00	5.0	5:15	10.0	5.0	6:45	61.5	81.4	94.5
14	2.5	0:12	- -	- -	7.5	3:45	10.0	2.0	3:57	58.5	79.9	98.5
15	2.5	0:13	1.0	1:00	7.5	3:45	10.0	3.0	4:58	58.8	79.9	97.5
16	2.5	0:13	2.0	1:00	7.5	4:20	10.0	4.0	5:33	59.2	80.0	96.5
17	2.5	0:12	3.0	1:00	7.5	4:35	10.0	5.0	5:47	59.5	80.0	95.0
21	5.0	0:36	- -	- -	7.5	6:46	12.5	2.5	7:22	61.4	83.0	98.4
22	5.0	0:33	2.0	1:00	7.5	6:29	12.5	4.5	8:02	62.5	83.0	96.0
23	5.0	0:30	3.0	1:00	7.5	8:53	12.5	5.5	10:23	63.0	82.3	95.6
26	7.5	1:26	- -	- -	7.5	8:01	15.0	3.0	9:27	64.1	83.4	98.1
27	7.5	1:33	2.0	1:00	7.5	8:34	15.0	5.0	11:07	66.0	82.9	94.9
28	7.5	1:26	3.0	1:00	7.5	9:03	15.0	6.0	11:29	66.1	83.2	94.8
32	7.5	1:15	3.0	1:00	10.0	10:32	17.5	6.3	12:47	66.7	83.2	93.9

Notes: (1) Percent chlorine used denotes active chlorine in hypochlorite based on o.d. unbleached pulp.
(2) Brightness denotes reflectance at an average effective wavelength of 457 millimicrons.
(3) Yellowness denotes reflectance at an average effective wavelength of 606 millimicrons.
(4) Percent Yield is based on o.d. unbleached pulp.

SUMMARY OF RESULTS

Combination of Various

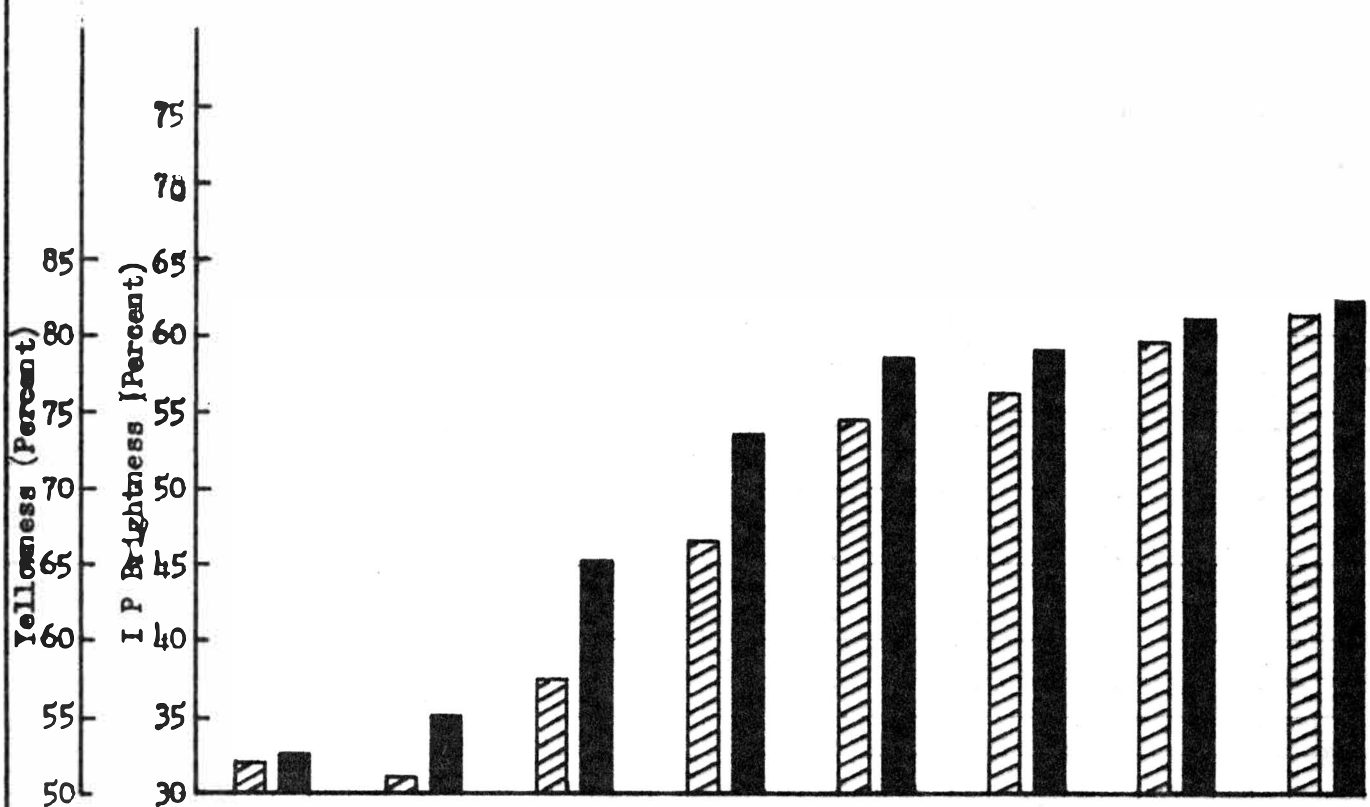
Bleaching Agents

Identification	Calcium Hypochlorite Treatment				Acidification		Hydrogen Peroxide Treatment		Zinc Hydrosulphite Treatment		Final Results		
	Chlorine Used Percent	Brightness Obtained Percent	Yellowness Obtained Percent	Yield Percent	Brightness Obtained Percent	Yellowness Obtained Percent	Brightness Obtained Percent	Yellowness Obtained Percent	Brightness Obtained Percent	Yellowness Obtained Percent	Final Brightness Percent	Final Yellowness Percent	Final Yield Percent
33	--	--	--	--	--	--	47.1	69.8	--	--	47.1	69.8	94.2
34	--	--	--	--	--	--	--	--	31.8	52.8	31.8	52.8	99.3
35	--	--	--	--	--	--	47.1	69.8	46.1	68.5	46.1	68.5	94.0
36	--	--	--	--	32.1	52.8	47.7	70.3	--	--	47.7	70.3	95.5
37	--	--	--	--	32.1	52.8	--	--	32.4	53.0	32.4	53.0	98.2
38	--	--	--	--	32.1	52.8	47.7	70.3	47.5	67.4	47.5	67.4	95.0
39	10	53.5	78.0	98.5	--	--	63.6	82.8	--	--	63.6	82.8	93.5
40	10	53.5	78.0	98.5	--	--	--	--	54.2	76.0	54.2	76.0	97.2
41	10	53.5	78.0	98.5	--	--	63.6	82.8	63.9	80.6	63.9	80.6	93.6
42	10	53.5	78.0	98.5	53.8	79.1	68.9	83.2	--	--	68.9	83.2	94.6
43	10	53.5	78.0	98.5	53.8	79.1	--	--	53.8	75.3	53.8	75.3	98.0
44	10	53.5	78.0	98.5	53.8	79.1	68.9	83.2	66.2	80.5	66.2	80.5	93.7
45	15	60.8	80.2	98.0	60.6	80.3	71.4	82.6	--	--	71.4	82.6	93.3
46	15	60.8	80.2	98.0	60.6	80.3	71.4	82.6	69.1	80.4	69.1	80.4	93.0
47	7.5 7.5	64.8	82.0	98.1	64.3	81.7	73.6	83.1	--	--	73.6	83.1	94.6
48	7.5 7.5	64.8	82.0	98.1	64.3	81.7	73.6	83.1	71.1	81.9	71.1	81.9	93.2

Notes:
(1) Percent chlorine denotes active chlorine in hypochlorite based on o.d. unbleached pulp.
(2) Brightness denotes reflectance at an average effective wavelength of 457milli microns.
(3) Yellowness denotes reflectance at an average effective wavelength of 606milli microns.
(4) Percent yield is based on o.d. unbleached pulp.
(5) Brightness of unbleached pulp: 32.0 percent.
(6) Yellowness of unbleached pulp: 52.5 percent.

Fig. 1

SINGLE STAGE BLEACHING WITH CALCIUM HYPOCHLORITE



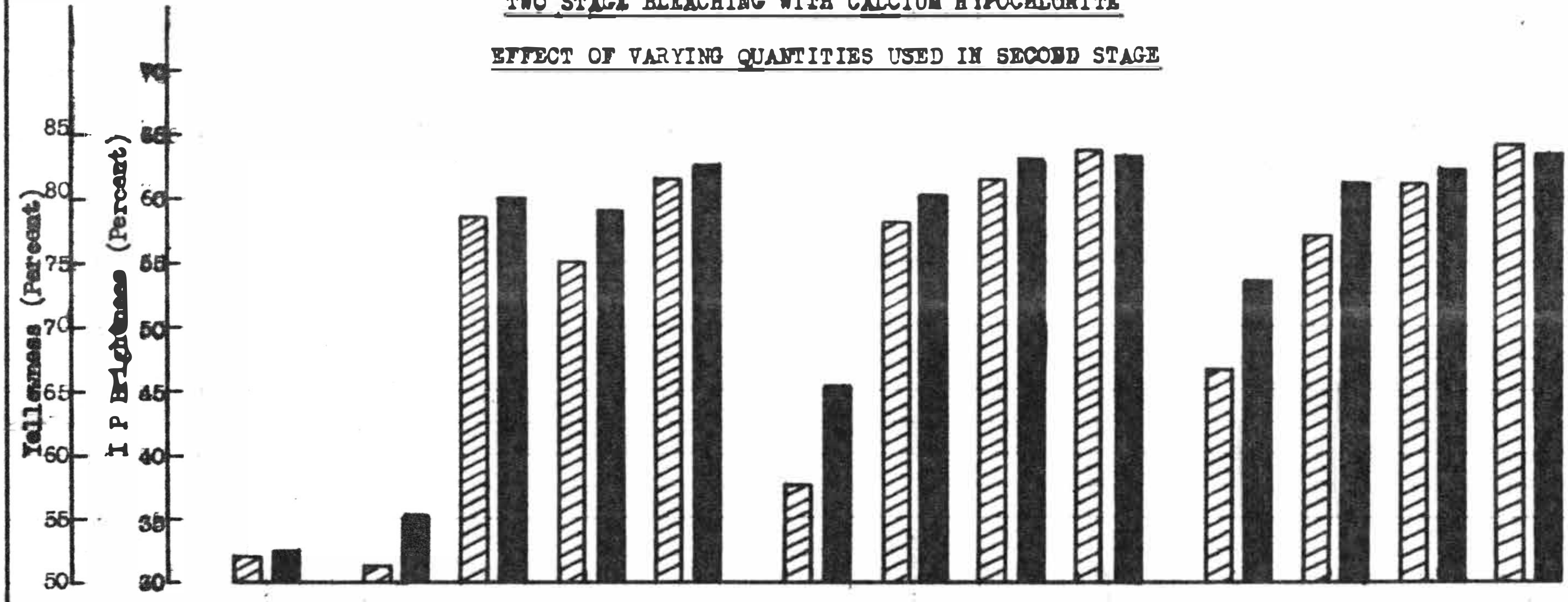
Identification	0	1	2	3	4	19	25	31
Chlorine used %	0	2.5	5.0	7.5	10.0	12.5	15.0	17.5
Yield %	100	99.3	99.2	99.0	98.4	98.5	98.0	98.7

I P Brightness

Yellowness

TWO STAGE BLEACHING WITH CALCIUM HYPOCHLORITE

EFFECT OF VARYING QUANTITIES USED IN SECOND STAGE

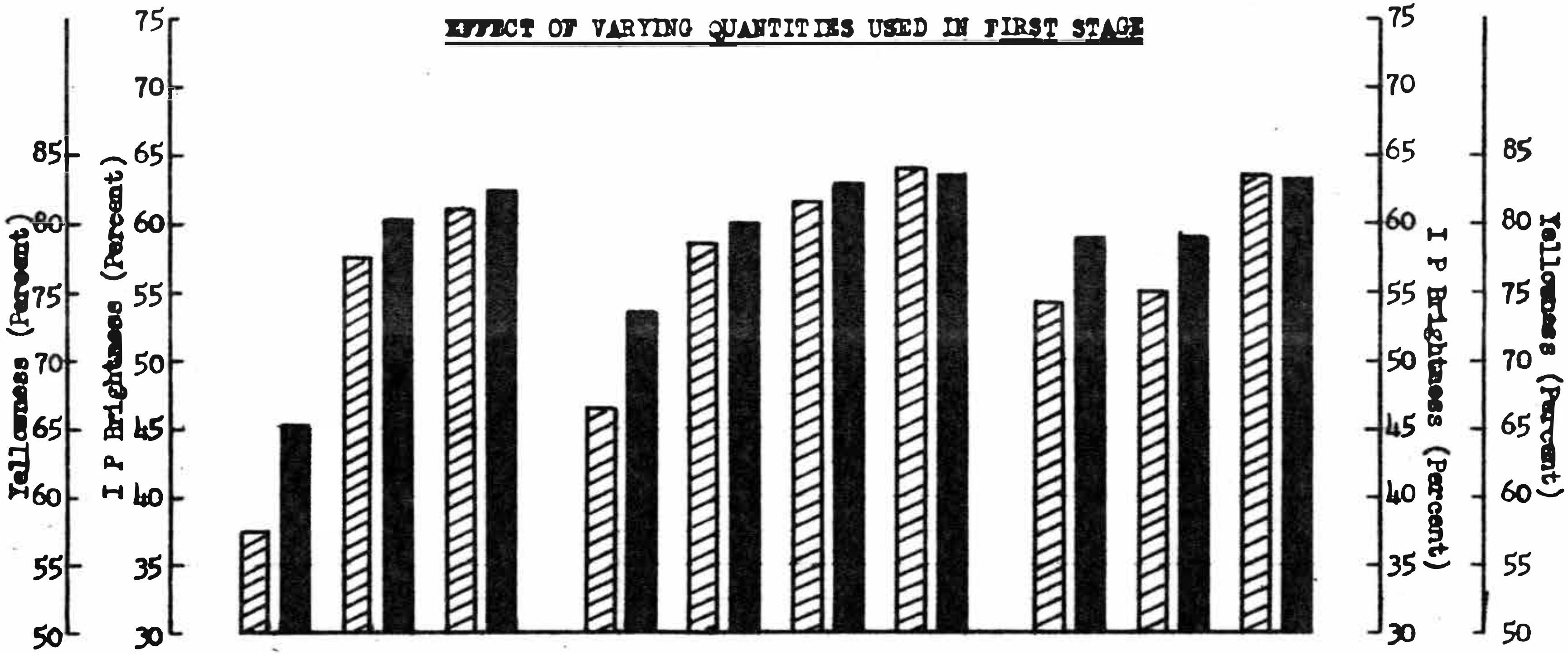


Identification		0	1	14	24	30	2	9	21	29	3	5	20	26
1st. Stage	$\%Cl_2$	0	2.5	2.5	2.5	2.5	5.0	5.0	5.0	5.0	7.5	7.5	7.0	7.5
2nd. Stage	$\%Cl_2$	0	0	7.5	10.0	12.5	0	5.0	7.5	10.0	0	2.5	5.0	7.5
Yield	%	100	99.3	98.5	98.1	97.9	99.2	96.8	98.4	97.9	99.0	98.0	98.6	98.1

Fig. 2

TWO STAGE BLEACHING WITH CALCIUM HYPOCHLORITE

EFFECT OF VARYING QUANTITIES USED IN FIRST STAGE



Identification		2	9	20	3	14	21	26	4	24	29
1st. Stage	$\%Cl_2$	5.0	5.0	7.5	7.5	2.5	5.0	7.5	10.0	2.5	5.0
2nd. Stage	$\%Cl_2$	0	5.0	5.0	0	7.5	7.5	7.5	0	10.0	10.0
Yield	%	99.2	96.8	98.6	99.0	98.5	98.4	98.1	98.5	98.1	97.9

I P Brightness (hatched)

Yellowness (solid)

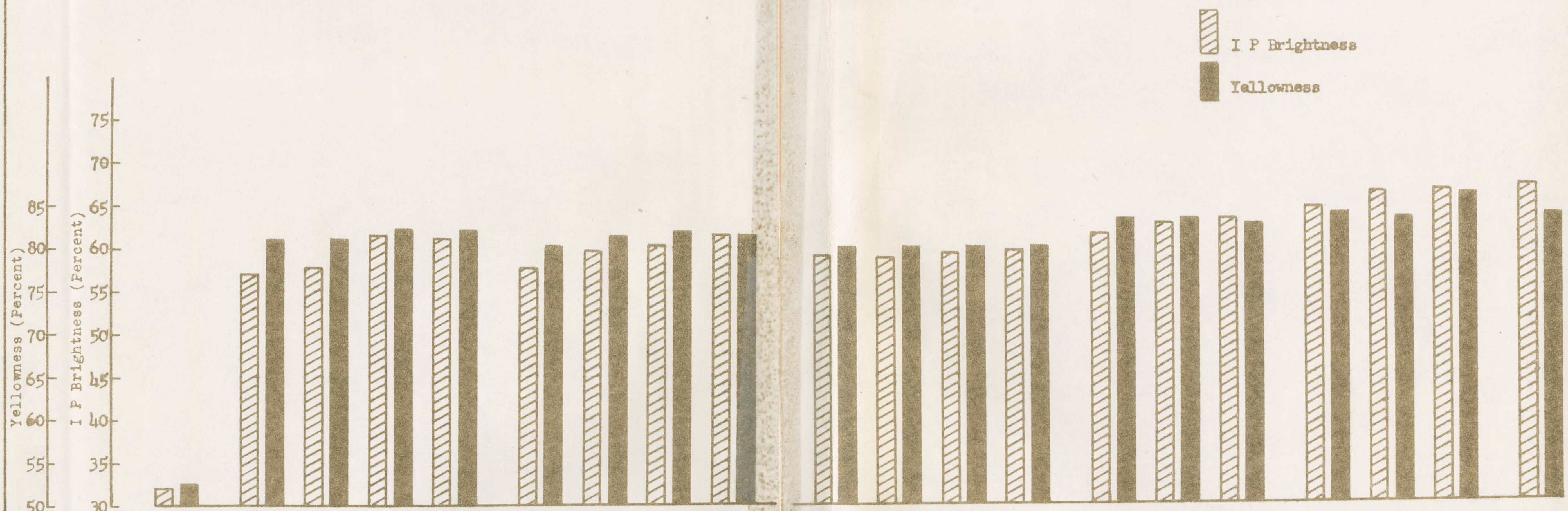
Fig. 5

Fig. 4

THREE STAGE BLEACHING

HYPOCHLORITE - CAUSTIC EXTRACTION - HYPOCHLORITE

THE EFFECT OF VARYING QUANTITIES OF
CAUSTIC SODA USED IN EXTRACTION STAGE

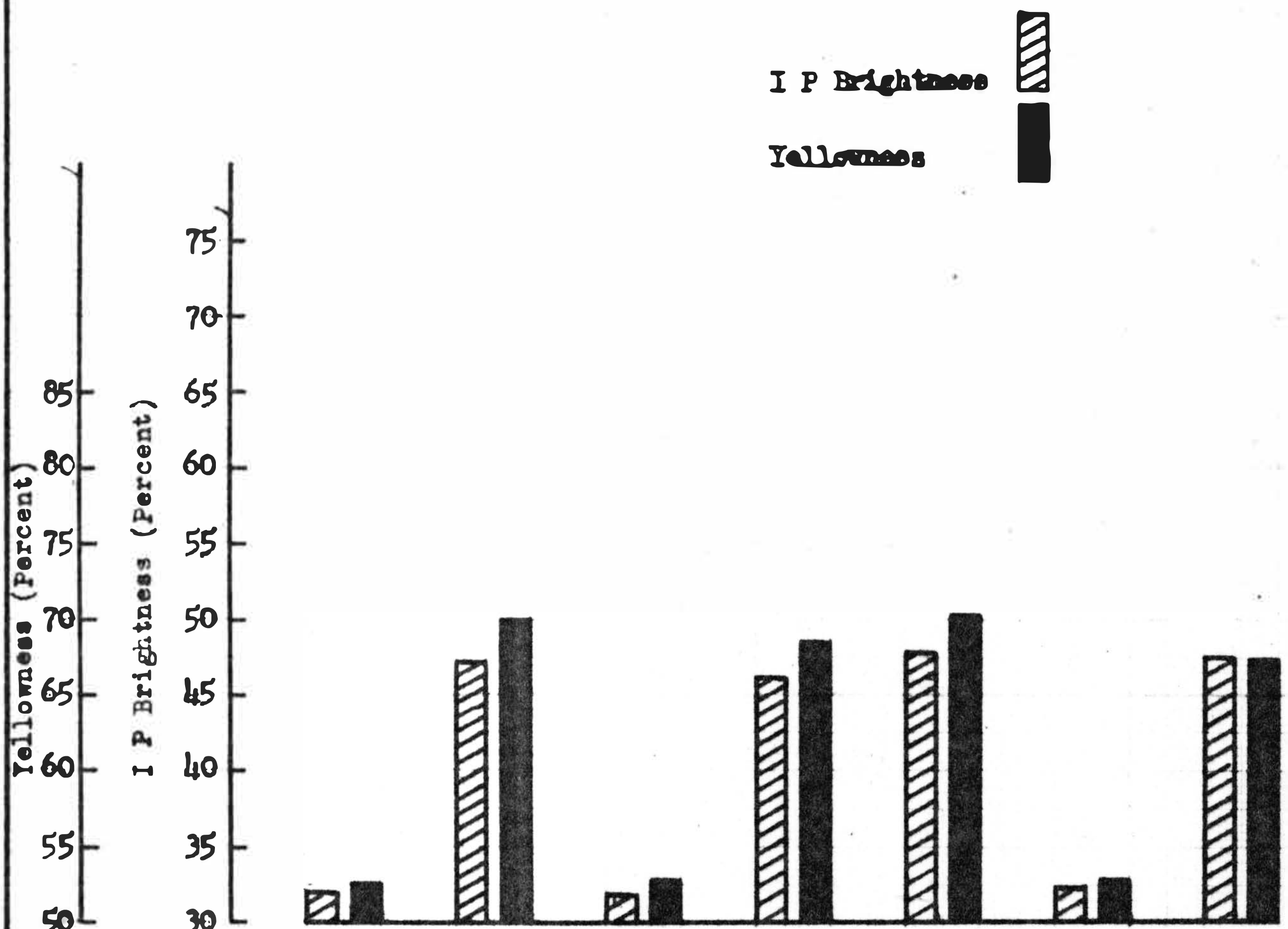


Identification	0	5	6	7	8	9	10	11	12	14	15	16	17	21	22	23	26	27	28	32
First Stage $\%Cl_2$	0	7.5	7.5	7.5	7.5	5.0	5.0	5.0	5.0	2.5	2.5	2.5	2.5	5.0	5.0	5.0	7.5	7.5	7.5	7.5
C. E. % NaOH	0	0	1.0	2.0	3.0	0	1.0	2.0	3.0	0	1.0	2.0	3.0	0	2.0	3.0	0	2.0	3.0	3.0
Sec. Stage $\%Cl_2$	0	2.5	2.5	2.5	2.5	5.0	5.0	5.0	5.0	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	10.0
Yield %	100	98.0	96.8	96.0	93.5	96.8	97.5	95.5	94.5	98.5	97.5	96.5	95.0	98.4	96.0	95.6	98.1	94.9	94.8	93.9

Fig. 5

THE EFFECT OF PEROXIDE AND HYDROSULPHITE

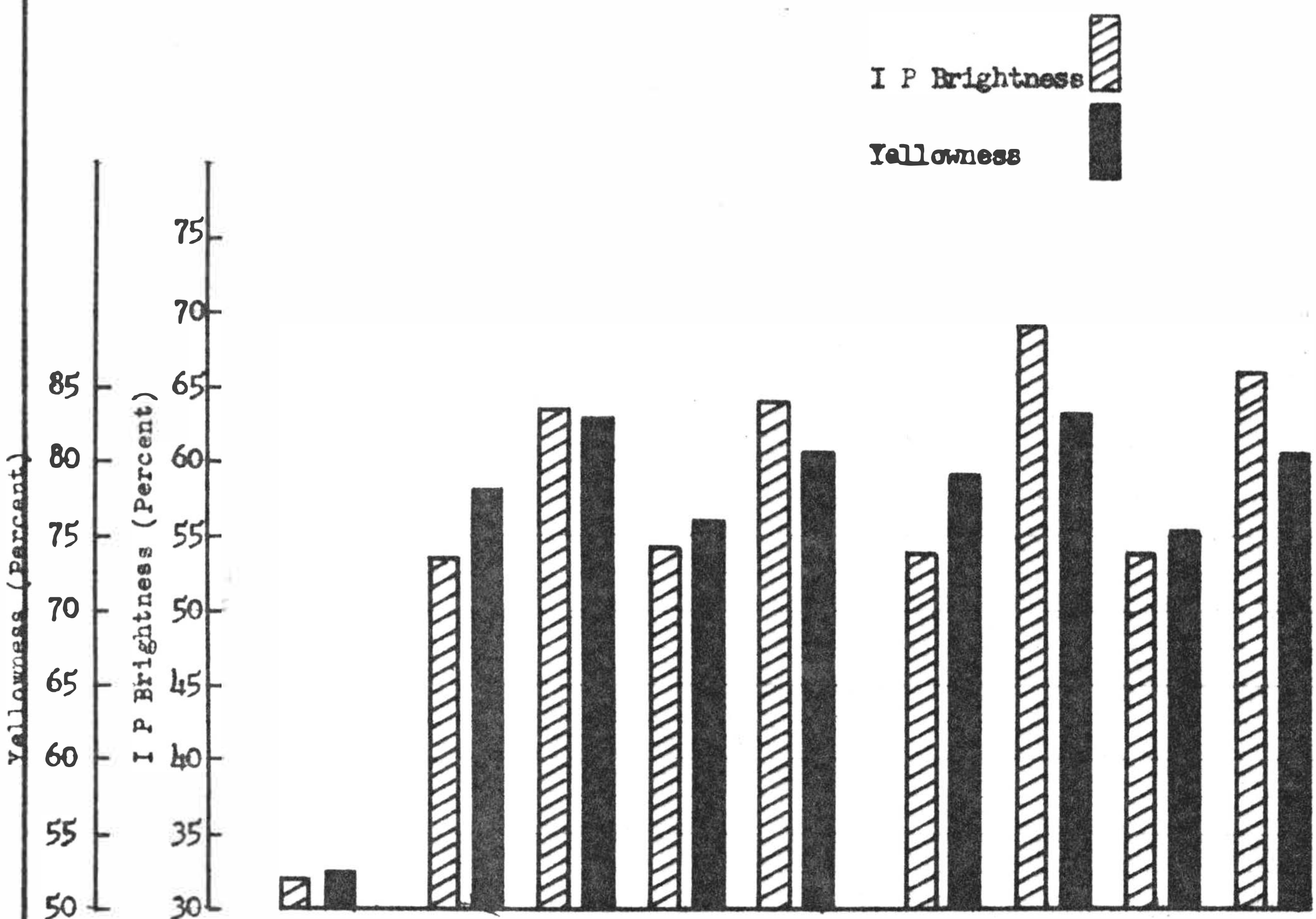
ON UNBLEACHED PULP



Identification		0	33	34	35	36	37	38
Acidification		No	No	No	No	Yes	Yes	Yes
H_2O_2 (50%)	%	0	2.6	0	2.6	2.6	0	2.6
Zinc Hydrosulphite	%	0	0	1.0	1.0	0	1.0	1.0
Yield	%	100	94.2	99.3	94.0	95.5	98.2	95.0

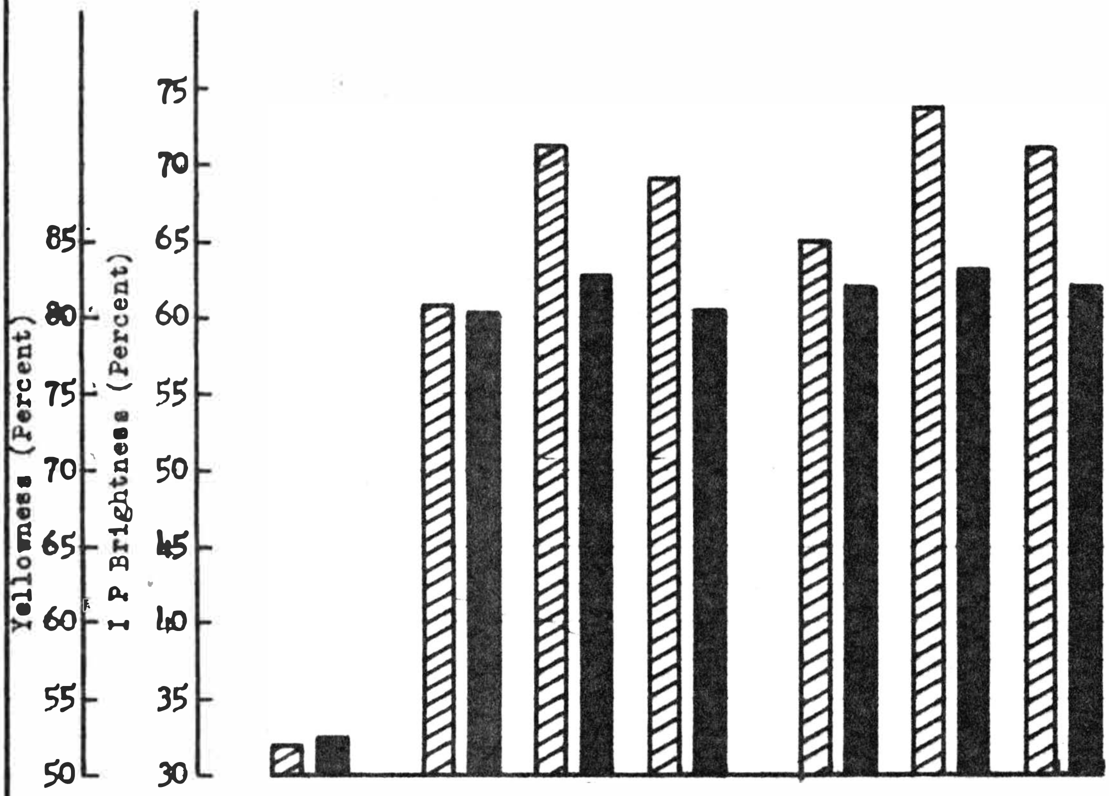
Fig. 6

THE EFFECT OF PEROXIDE AND HYDROSULPHITE ON HYPOCHLORITE BLEACHED PULP



Identification	0	4	39	40	41	4	42	43	44
% Cl_2 as Hypo	0	10	10	10	10	10	10	10	10
Acidification	No	No	No	No	No	Yes	Yes	Yes	Yes
H_2O_2 (50%) %	0	0	2.6	0	2.6	0	2.6	0	2.6
Zn Hydrosulphite %	0	0	0	1.0	1.0	0	0	1.0	1.0
Yield	100	98.5	93.5	97.2	93.6	98.5	94.6	98.0	93.7

THE EFFECT OF PEROXIDE AND HYDROSULPHITE ON HYPOCHLORITE BLEACHED PULP



Identification	0	25	45	46	26	47	48
% Cl_2 as Hypo	0	15.0	15.0	15.0	15.0*	15.0*	15.0*
Acidification	No	No	Yes	Yes	No	Yes	Yes
H_2O_2 (50%)	0	0	2.6	2.6	0	2.6	2.6
Zn Hydrosulphite	0	0	0	1.0	0	0	1.0

(*) Chlorine used in two stages, each of 7.5% chlorine as Ca-Hypochlorite

I P Brightness

Yellowness

BLEACHING OF HIGH YIELD N.S.S.C.

PULP AS RECEIVED

REFINED, SCREENED & CENTRICLEANE
PULP.

32% BRIGHTNES

10% CHLORINE

4.3% BRIGHTNESS

5% CHLORINE
.6% H_2O_2

.6% BRIGHTNES