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The Performance of Sodium Hypochlorite and Sodium Hypobromite as Bleaching Agents at Varying Levels of Hydrogen Ion Concentration

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THE PERFORMANCE OF SODIUM HYPOCHLORITE AND SODIUM HYPOBROMITE AS BLEACHING AGENTS AT VARYING LEVELS OF HYDROGEN ION CONCENTRATION.

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ABSTRACT

Limited information was found in literature survey on the bleaching of wood pulp by means of hypobromites. Experimentation showed that the addition of sodium bromide to sodium hypochlorite results in accelerated bleaching. The optimum pH range for bleaching was found to be higher in presence of hypobromites than in straight hypochlorite bleaching. The maximum brightness values obtained in bleaching with either straight sodium hypobromite or with mixtures of hypochlorite and hypobromites were lower than those obtained with sodium hypochlorite.

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Literature Survey

The objective of the survey has been an attempt to secure the information that had been published on the influence of the variation of pH values on the single stage bleaching of pulp with sodium hypochlorite and sodium hypobromite. Much has been written on this subject in connection with hypochlorites, but the literature pertaining to bleaching with hypobromite is very scanty.

Hypochlorites as Single Stage Bleaching Agents

In the wet processing of cellulose materials by means of hypochlorite solutions it is now known that the results obtained depend to an important extent on the hydrogen-ion concentration of the mixture. When chlorine is dissolved in water the reaction may be represented as follows:

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$

When the pH is below 2 the equilibrium is shifted sharply to the left, but as the pH is raised by addition of an alkali it shifts toward the right, and at about pH 5 the concentration of HOCl is at a maximum. Further increase of pH may be represented by the following reaction, in which an increase in pH again shifts the equilibrium to the right:

$$HOCl + NaOH \rightleftharpoons NaOCl + H_2O$$

The products formed on dissolving chlorine in water depend, then, on the pH and the changes in composition, which take place with changes in pH, are reversible. The following table as presented by Sutermeister[1] summarizes roughly the equilibrium conditions:

TABLE I

Equilibrium Conditions of Chlorine, Hypochlorous Acid and Hypochlorites

Below pH 2	Chlorine present predominatly as elemental chlorine.
pH 2-3	Elemental chlorine present along with hypochlorous acid.
pH 4-6	Hypochlorous acid predominates.
pH 7-9	Hypochlorous acid present along with hypochlorite.
Above pH 9	Chlorine present predominatly as hypochlorite.

As the hypochlorites may react with cellulose as well as with the impurites accompanying it, it is important to select such conditions of reaction that the chemical attack is chiefly on the impurities rather than on the cellulose. If the pH falls below 7.5 or 8.0 for a major portion of the bleaching period three undesirable conditions may prevail: (a) a portion of the available chlorine may react by chlorination; (b) a portion of the hypochlorous acid which is present under these pH conditions, may be lost by volatilization or by decomposition, in which ease the residual chlorine may not be sufficient to effect the desired brightening of the pulp;

or (c) the hypochlorous acid may react so rapidly that the cellulose will be attacked and the fibers lose strength. For these reasons it has been found desirable in many commercial operations to raise the pH of the bleaching mass by the addition of lime or caustic soda.

During bleaching the alkaline hypochlorites break down to form the hypochlorite-ion, and some elemental chlorine, depending upon the pH of the bleach bath. Alkaline pH is more favorable to hypochlorite-ion formation with subsequent oxidation of the lignin in pulp. It is this oxidation process which tends to "whiten" or "bleach" the pulp. As the bleaching reaction progresses the pH drops due to formation of carbon dioxide and other acidic materials. Several investigators have shown that, when the bleaching operations with hypochlorite is carried out at a pH from 6 to 8, maximum degradation of the cellulose occures, as measured by low strength of the fibers and low viscosity of solutions of the cellulosic material.(2)

In experiments conducted by Casciani and Storin(3) successful attempts were made to obtain information of practical value regarding the effect of pH on chlorine consumption, on bleaching time, and on chemical as well as physical properties of the pulp. All pulp specimens were bleached to practically the same degree of brightness. The results of these experiments showed in general that the higher the final pH value, the lower the amount of available chlorine required to obtain the same brightness of pulp.

In the range of pH values of 5.8 to 6.5 there was an unexpected increase in chlorine requirement for which no satisfactory explanation could be found. No significant saving in chlorine was effected by employing final pH values higher than 9.0. Increasing the final pH above 7.4 resulted in a rapid lengthening of the bleaching time. Between the final pH of 6.0 and 7.0 there was a greater increase in bleaching time than in the pH range of 3.0 to 6.0.

In spite of the practically identical brightness obtained in all tests, the pulps bleached at the lower pH values appeared whiter to the eye. Colorimetric measurements revealed that the pulp bleached at the lower pH was nearly neutral white in color. The ash content of the pulp increased as the final pH during bleaching increased. The alpha-cellulose content showed a gradual but persistent increase as the final pH was raised from 4.0 to 9.0. Below a pH of 4.0 there was a marked decrease in alpha-cellulose content. The pulps bleached at lower pH values were the least subject to fading. The pH of bleaching appeared to have little effect on the strength properties of the pulp so long as the pulp was bleached to the same brightness in every case.

Hypobromites as Single Stage Bleaching Agent

As mentioned before, the information on pulp bleaching with hypobromites is very limited but laboratory and mill experiments have been described for bleaching pulp with the addition of calcium bromide in the hypochlorite stage. Advantages were claimed such as a somewhat stronger pulp with higher alpha cellulose content and lower copper number, heat economies, and a shorter bleaching period. The disadvantages include a somewhat higher pitch and ash content as well as poorer cleanliness of the pulp.(4) More detailed information on hypobromite bleaching is available through research by H. W. Giertz.(5) At the present time it is impossible to have this information due to the absence of an abstract of his work in several of the standard sources. In addition experiments have been conducted involving rates of oxidation of cellulose by hypobromite and hypochlorite-bromide mixtures have been determined at various pH values.

In presence of hypobromites the rates of oxidation of bleached wood pulp, bleached cotton, bleached flax, and viscose yarns increase with increase in pH, contrary to oxidations with hypochlorite. The composition and behavior of hypochlorite and bromide mixtures are governed by the rates of the reactions between hypochlorites and bromides yielding hypobromite at pH values 9-13 and hypobromite, bromate, bromite, chlorite and chlorate at the pH values 7-9. This is shown by the following equations:

$$ClO^- + Br^- = OBr^- + Cl^-$$

The rates of this reaction decrease with increasing pH and takes for its completion from several minutes (pH range 9-10) up to several hours (pH 12-14). At lower pH values, a series of other reactions take place simultaneously; these have not been thoroughly investigated, but can be formulated schematically as follows:

$$2ClO^- + BrO^- = 2Cl^- + BrO_3^-$$

$$ClO^- + 2HClO = 2H^+ + 2Cl^- + ClO_3^-$$

$$BrO^- + 2HClO = BrO_3^- + 2H^+ + 2Cl^-$$

The rate of these reactions increase with decreasing pH.(7)

The properties of the hypobromite oxycelluloses have been determined. The viscosities in cuprammonium solution increase with decreasing pH of the oxidation runs, and the "dangerous zone" known in the hypochlorite oxidations at pH 7 is not found here; maximum of reducing groups is observed at pH 8-9. The decrease in these groups at the higher pH values is accompanied by a corresponding increase in carboxyl groups. This suggests that the reducing groups are formed through the action of the hypobromous acid where as the carboxyl groups are formed through the action of hypobromite-ions. The results obtained point to new possibilities of bleaching cellulosic materials with hypobromite and hypochlorite-bromide mixtures.(6)

A translation of the Swedish article by Nordlund (4) may be found at the end of the thesis.

THE EXPERIMENTAL INVESTIGATION

Three different solutions were used as single stage bleaching agents. These were:

1. Sodium hypochlorite
2. Sodium hypochlorite in prescence of sodium bromide
3. Sodium hypobromite

PREPARATION OF BLEACHING AGENTS

The sodium hypochlorite was prepared by passing chlorine gas through a cold solution of sodium hydroxide. The resultant solution had a strength of 44.5 grams of chlorine per liter.

The sodium hypobromite was prepared by adding, slowly with stirring, elementary bromine to a cold solution of sodium hydroxide. The temperature was kept below 15^{o} C. The resultant solution had a strength of 100 grams of bromine per liter.

The concentration of the bleaching solutions was established by titration with sodium thiosulphate.(8)

EXPERIMENTAL PROCEDURE

The bleaching experiments were conducted in the following manner:

Consistency----------3.8 percent

Temperature----------44±1° C.

Chlorine consumption--------3.48 grams per one hundred grams of oven dry pulp, which is equal to .049 moles of chlorine.

Bromine consumption - 7.8 grams per one hundred grams of oven dry pulp. Which is equal to 0.49 moles of bromine.

Pulp used----------Unbleached sulfite (Saint Raymond)

Bleaching Procedure Used with Sodium Hypochlorite.

One hundred milliters of distilled water and twenty milliters of bleach liquor were placed in a beaker. The hydrogen ion concentration of the solution was then adjusted with normal hydrochloric acid, additional water was added, and the pH checked. The solution was then poured over eleven grams of moist pulp (eight grams oven dry) in an eight ounce bottle. This gave a total volume of 210 milliters. The bottle was then placed in a water bath at 44±1° C. and the bleaching action was allowed to proceed. At certain intervals a five milliter portion of the contents of the bottle was removed and the residual chlorine content determined. When the specified amount of chlorine was consumed, the bleaching procedure was stopped by placing the pulp in a Buchner funnel and washing it thoroughly with distilled water.

The resultant pad was pressed and allowed to dry in a constant humidity room. Bleaching runs were made at pH values of four, six, seven, eight and ten. Brightness, bleaching time, and final pH were recorded.

Bleaching Procedure Used with Hypo chlorite-Bromide Mixtures

This procedure was identical with the one used in bleaching experiments with hypochlorite except that a solution of sodium bromide was added to the bleach liquor in order to observe the effect of small amounts of hypobromite on hypochlorite solutions. The sodium bromide solution contained 3.3 grams of the salt per liter. Ten milliliters of this solution was added to the bleach liquor in place of ten milliliters of water. This quantity of sodium bromide was recommended in the literature.(4) Bleaching runs were limited to pH values of six, seven, eight, nine and ten.

Bleaching Procedure for Hypobromites

The procedure in this case is the same as the one used in bleaching with hypochlorites. Bleaching runs were carried out at pH values of eight, nine, ten and eleven.

OBSERVATIONS

It was noticed that due to presence of hypobromite in the bleaching experiments, the solutions became increasingly unstable with decreasing pH. Thus, sodium hypochlorite was relatively stable to a pH value of four before noticeable quantities of elemental chlorine were produced. At a pH value of six, chlorine and small amounts of bromine appeared in the hypochlorite containing some sodium bromide. Straight sodium hypobromite was the least stable compound; below a pH value of eight, bromine was liberated. In view of these observations experiments were discontinued in these ranges of pH where quantities of elemental chlorine and bromine were evolved.

EXPERIMENTAL RESULTS

The following table shows the data obtained with the procedure and agents previously described. Data are ploted in figure one which shows the relationship of bleaching pH versus bleaching time. Figure two graphically illustrates the results of brightness attained versus bleaching pH.

DATA

Bleaching agent-----Sodium Hypochlorite

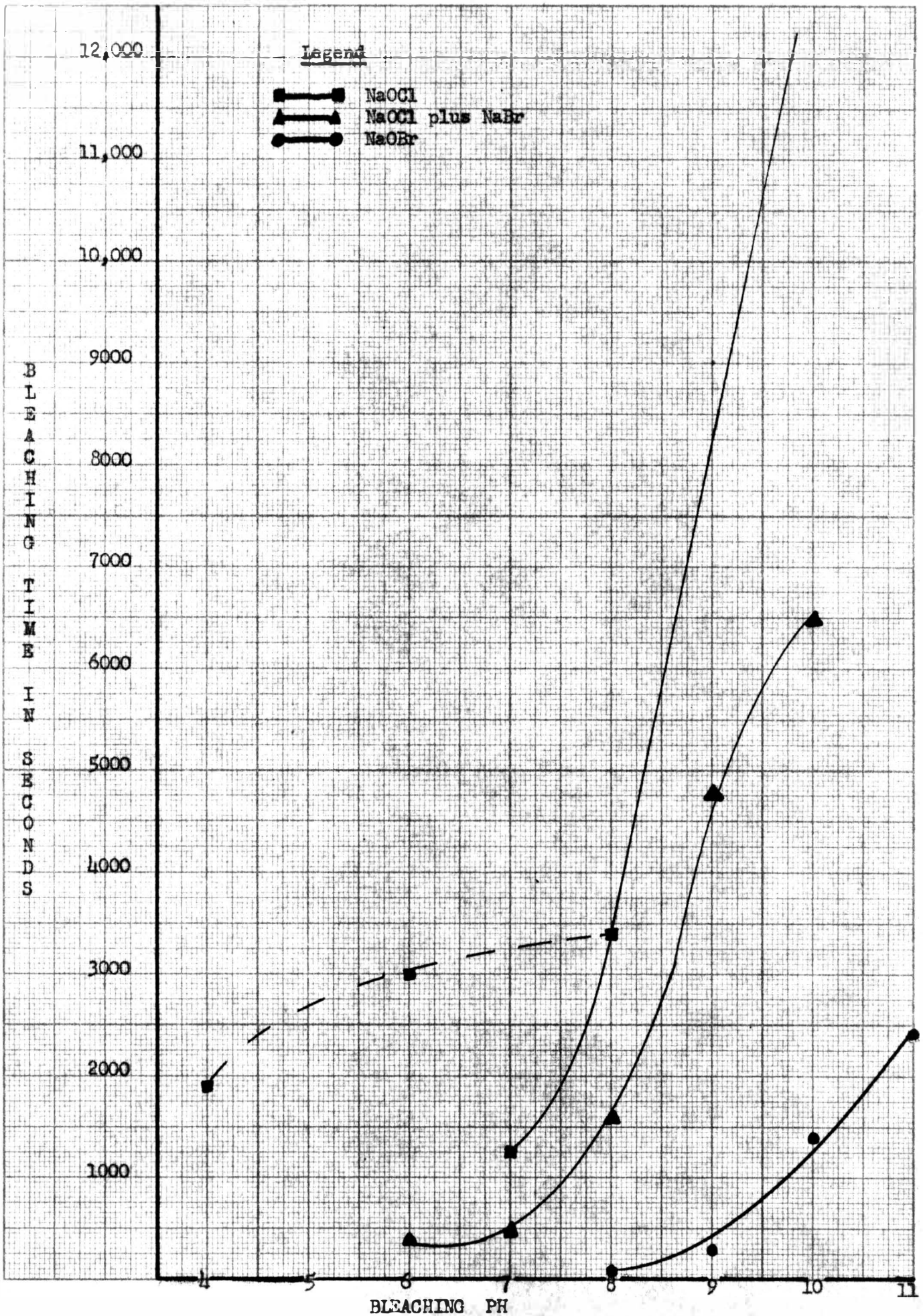
PH		BRIGHTNESS	BLEACHING TIME IN SECONDS
Inital	Final		
4	3.7	72.5	1930
6	4.0	77.0	3000
7	6.4	81.5	1250
8	6.4	82.5	3400
10	6.4	83.0	13,000

Bleaching agent-----Sodium Hypochlorite plus Sodium Bromide

6	3.7	64.0	400
7	7.3	74.0	500
8	6.4	80.0	1600
9	8.1	82.5	4800
10	6.6	82.5	6500

Bleaching agent-----Sodium Hypobromite

8	7.6	65.0	110
9	8.5	73.0	300
10	9.3	80.0	1400
11	9.5	81.0	2400


Legend
NaOCl
NaOCl plus NaBr
NaOBr
12,000
11,000
10,000
9000
8000
7000
6000
5000
4000
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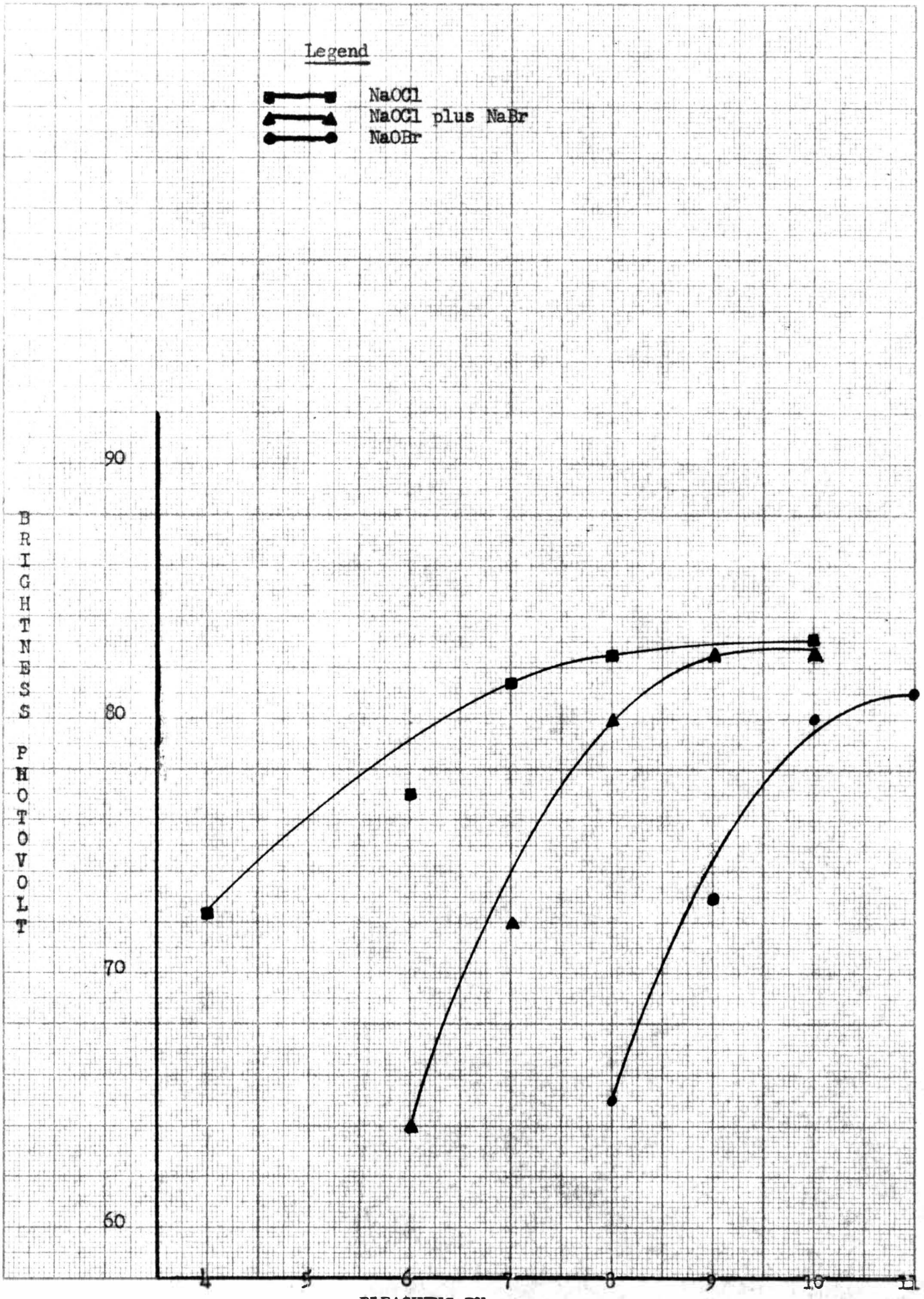
2000
1000
BLEACHING TIME IN SECONDS
4
5
6
7
8
9
10
11
BLEACHING PH


Legend
NaOCl
NaOCl plus NaBr
NaOBr
BRIGHTNESS PHOTOVOLT
90
80
70
60
4
5
6
7
8
9
10
11
BLEACHING PH

INTERPRETATION OF DATA

As a result of the experimental data it appears that in the presence of hypobromite, hypochlorites produce a relatively low brightness in the pH range of four to eight. Above this range Photovolt brightness values of above eighty were obtained, which is very close to that of the standard hypochorite bleachings. With increasing pH the bleaching time of both hypochlorites and hypochlorite-bromide increased very rapidly but in the presence of hypobromites, hypochlorites showed substantially reduced bleaching time. The rapid consumption of the active constituent of sodium hypobromite in the pH range of eight to eleven limited the maximum brightness to eighty one percent and below a pH value of ten the brightness decreased rapidly.

CONCLUSIONS

The addition of sodium bromide to sodium hypochlorite results in accelerated bleaching. The optimum pH range for bleaching was found to be higher in presence of hypobromites than in straight hypochlorite bleaching. The maximum brightness values obtained in bleaching with either straight sodium hypobromite or with mixtures of hypochlorite and hypobromites were lower than those obtained with sodium hypochlorite.

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APPENDIX

Hypochlorite Bleaching of Sulphite Pulp

with

Addition of Calcium Bromide

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Hypochlorite Bleaching of Sulphite Pulp with Addition of Calcium Bromide

Some years ago the sulphite mill of W. Rosenlew and Co. in Bjorneborg was visited by Dr. Schnerb from Palestina Potash. Co. During his visit the possibilitys of useing bromides as an bleaching additive with sulphite pulp were discussed. According to Dr. Schnerb the advantages of adding bromide salts to the bleaching operation were as follows;

Tensile strength and folding endurance would be improved. The bleaching time would be shortened to ond third of the normal time. If a case should arise where there were technical reasons that the bleaching time should not be shortened, the bleaching temperature may be reduced to 25° C. If a lower temperature is derired , the amount of bromide added may be reduced. The combination of both alternitives may be considered. At a bleaching temperature of approximately 40° C. the amount of calcium bromide added may not be larger than 3.3 Kg. per ton of pulp. Alkali may be saved by holding the bleaching pH in a lower range with bleach and bromide mixtures than with normal hypochlorite. According to some conclusions drawn 3.5 Kg. of sodium hydroxide per ton of pulp may be saved in one hypochlorite step. Further more Dr. Schnerb persented several diverse cost calculations according to which it would be economically advantagous to add calcium bromide in bleaching operations.

These calculations are of theoretical interest and are not applicable in every case because many local variant factors effect production costs. On the basis of these discussions several bleaching experiments were carried out.

In the laboratory test the bleaching experiments were conducted in the following manner;

Chlorination was accomplished at room temperature by means of chlorine water at a pulp consistency of 1.5 percent. To this pulp was added 65 percent of the total chlorine required (based on bleachability) and the rest was introduced in the hypochlorite step. Alkaline treatment was carried out at room temperature with the addition of 0.6 percent sodium hydroxide at a 9 percent pulp consistency for 120 minutes. Hypochlorite treatment was carried out in a water bath at 40° C. with a pulp consistency of 5.5 percent for five to eighteen hours. The The hypochlorite bleach used contained 20 to 22 grams of chlorine per liter. Between each operation the pulp was pressed and washed. Addition of the bromide salt can be done intermittently or continously one to two hours after the addition of the hypochlorite bleach. For comparsion of results samples of the same pulp were bleached under the conditions without the bromide addition.

Results of the Laboratory Experiments

1. The bleaching time was reduced 40 to 50 percent without affecting the bleaching results.

2. The bleaching temperature can be reduced from eight to ten degrees Centigrade below the forty degrees Centigrade set as a standard.

3. Residual chlorine will lowered so the risk of the mass yellowing after bleaching is reduced.

How much of the yellowing of the pulp is caused by the residual bromide salt has not been determined but the amount of bromide salt added to the bleaching mass should not be more than four tenths of a percent based on oven dry pulp. Larger amounts will bring poorer brightness. Smaller amounts will give no noticable results.

4. The pH is reduced sooner, but the resulting pH can be held higher without the use of alkali.

5. The alpha-cellulose content is higher and the copper number lower.

6. The whiteness is lowered.

7. Cleanliness became poorer.

8. The viscosity is increased.

9. The ash and pitch content were increased.

Results of Mill Experiments

Through the courtesy of Palestina Potash several 40 Kg. drums of calcium bromide were obtained. This technical grade of bromide salt

contained ten percent water and was the material used in the seven experimental bleachings that were carried out in the mill. These operations were carried out in duplicate in the same manner as in the laboratory. Of the experiments conducted no definite conclusions can be drawn but the following results in each case should be considered.

1. The bleaching temperature can be reduced from three to four degrees.
2. The bleaching time was shorteded about 50% without affecting the bleaching results.
3. The alpha-cellulose became 0 to 5.9 percent higher and the copper number was decreased.
4. Whiteness was lowered.
5. Cleanliness became poorer.
6. Viscosity became higher.
7. Some bleachings were beaten in a Valley-Hollender by means of which the tensile strength was increased 40 to 1215 m. and the mullen 0.5 to 15.2 Kg./cm^2. Wear and elasticity remained about the same. The final bleaching pH of 7.8 gave the highest viscosity.
8. The ash content was higher and the increase in pitch was 0.1 to 0.25 percent.

The results of the mill experiments deffered from those in the labrotory. These variations are probably due to several of the following conditions:

1. The pulp used was freshly prepared.
2. The experiments were made on a larger scale.
3. In place of potassium bromide technical calcium bromide was used.
4. The bleaching process in its self is different in some respects.