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Low Shrinkage Bleaching of Unbleached Neutral Sulphite Semichemical Pulp

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LOW SHRINKAGE BLEACHING OF
UNBLEACHED NEUTRAL SULPHITE SEMICHEMICAL PULP

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Summary

The main objective of this research project was the investigation of the most feasible method for the bleaching of a soft-cooked unbleached neutral sulphite semichemical aspen pulp cooked to a 70 percent yield. Futhermore,treatment of unbleached,laboratory bleached and commercially bleached neutral sulphite semichemical pulp with a new chemical, sodium borohydride,was also carried out.

The results of our experimental work showed that, the best bleaching procedure was when 15 percent chlorine as hypochlorite was used in the first stage,followed by a hydrochloric acid soaking stage with a final treatment of 2.6 percent hydrogen peroxide. With the above procedure brightness values over 80 percent were obtained with the yields in the 90 percent range based on the weight of the pulp. Sodium borohydride treatment of the three pulps showed that,with regards to ultra-violet light and heat stability the chemical,sodium borohydride,had no effect on the unbleached and the bleached lignin-containing pulps. Treatment of the commerically bleached,lignin-free,pulp however showed that the chemical had a marked effect in improving the heat and light stability of the pulp. It was noted that with all three types of pulp the chemical sodium borohydride did produce a bleaching effect.

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Literature Survey

Introduction

In recent years increasing attention has been given to the production and the use of a bleached hardwood pulp made by the neutral sulphite semichemical process. A pulp produced by this method has some advantages,for example, a neutral sulphite semichemical pulp can be produced in unbleached condition at a yield of about 75 percent based on the weight of the wood. The process also utilizes hitherto little used wood species,namely,some hardwoods which according to Trelfa (1) are now the growth pulp trees of the paper and board industry. This process does,however,have certain disavantages,the greatest being that the yield obtained after bleaching of the pulp to a relatively high brightness is materially reduced and that the cost of bleaching chemicals is relatively high. It must be realized,therefore,that in bleaching of this pulp the selection of a proper bleaching method is of the utmost importance in order to produce a pulp of good brightness with shrinkage as low as possible. This can be accomplished in theory by considering bleaching as a continuation of the pulping process, Therefore,adjusting the shrinkage by controlling the amount of residual lignin remaining after bleaching is important.

In actual production systems, it is sometimes advantageous to produce a bleached pulp containing some residual lignin and to employ certain selective bleaching agents which produces a pulp with optical properties of fully bleached fibers under minimum shrinkage conditions.

Objective

The main objective of this literature survey is to bring up to date a thesis prepared by Reinhardt (2) on bleaching of high yield neutral sulphite semichemical pulp and to report on new bleaching processes and chemicals used in bleaching high yield and groundwood pulps.

Bleaching of Neutral Sulphite Semichemical Pulp

Reinhardt (2) worked with a mechanically cleaned unbleached neutral sulphite semichemical pulp cooked to a yield of 78 percent based on wood and possessing a brightness value of 32 percent, measured on the I.P.C. brightness tester. Reinhardt's work showed the following results about the bleaching of neutral sulphite semichemical pulp with different variations in bleaching stages and agents.

The best brightness was obtained when 15 percent chlorine as calcium hypochlorite was split in equal parts between two stages. Using this quantity of chlorine he obtained a 32.8 point brightness gain with a shrinkage of merely 1.9 percent based on the weight of the unbleached pulp. Acidification of the pulp with a 2 percent sulfuric acid solution before treatment with hydrogen peroxide caused, in general, a decrease in the brightness with an increase in the yellowness. However, treatment of the pulp with 2.6 percent (50 percent solution) hydrogen peroxide producing a brightness gain of 8.8 points with a noticeable shrinkage of 5.4 percent based on the weight of the unbleached pulp. Further treatment of the pulp with 1.0 percent zinc hydrosulphite solution had no significant effect upon optical properties, except to reduce the yellowness a few points.

Nolan (3) worked with a Southern hardwood neutral sulphite semichemical pulp cooked to 65 percent yield with a brightness value of 34 percent. Treatment of the pulp with 10 percent hypochlorite in the first stage, with a 1.0 percent caustic extraction in the extraction stage, followed by 1.5 percent hydrogen peroxide (50 percent solution) in the third stage, resulting in a total brightness gain of 35.7 points with a shrinkage of 9.2 percent. All of the above percentages are based on the weight of the unbleached pulp.

Furthermore, Nolan (3) found that preliminary treatment of the pulp with sufficient hydrochloric acid to bring the pH level to 1.8 resulted in a slight increase in brightness but a very definite saving in peroxide. It was noted, also, by Nolan (3) that when sulfur dioxide (SO_2) water is used in forming brightness handsheets, a slight decrease in brightness was observed.

New Bleaching Agents

Mayer and Donofrio (4) treated unbleached mechanical pulp with sodium borohydride ($NaBH_4$) and observed a bleaching effect which was controlled by three variables: alkalinity, temperature,and consistency.

The most effective application of the chemical was to allow the unbuffered borohydride to seek its own pH level which was approximately 10.3. At this point maximum brightness could be realized. At a lower pH level,the reaction time was speeded up without any advantages as to the brightness gain. Increasing the temperature accelerated the chemical consumption but had a negative effect on the pulp brightness. The optimun temperature for best brightness and lowest corresponding chemical consumption was 35 C. Increasing consistency improved only the stability of the chemical.

Bleaching of mechanical pulps with sodium borohydride resulted in a definite advantage over pulp bleached with sodium peroxide and zinc hydrosulphite in reflectance in the 300 to 425 mu range. Over the remaining spectrum the bleaching action of borohydride was comparable to peroxide.

New Bleaching Process

In addition to conventional bleaching processes,it was announced by a manufacture of chemicals (5) that bleaching of high yield pulps,particularly cold caustic soda pulps, could be used successfully by introducing peroxide bleach during the refining operation typical for most high yield pulp processes. This method was said to produce pulps of substantially improved brightness without a bleach plant and with a minimum of auxiliary equipment.

Literature Cited

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Low Shrinkage Bleaching of Unbleached Neutral Sulphite Semichemical Pulp

Experimental Design

Objective

The main objective of this research project is to investigate the most feasible method for the bleaching of a soft-cooked unbleached neutral sulphite semichemical aspen pulp cooked to 70 percent yield.

Experimental Details

The experimental work shall consist of applying Reinhardt's (2) best bleaching procedure to the above pulp and comparing the effects which this procedure has upon the optical properties of the pulp. Modifications of this procedure will then be made to improve the results and to decrease the cost of the bleaching method by varying the amount of chlorine as hypochlorite in the first stage between 7.5 to 15 percent and in the second stage between 0 to 7.5 percent. Experiments will also be made with hypochloric and sulfuric acid used as an acid soaking stage preceding treatment with peroxide. The amount of hydrogen peroxide used in the last stage will be varied to a maximum of 2.6 percent. As an after-treatment sodium borohydride will be reacted with the pulp in quantities varying from 1 to 3 percent in order to investigate the possible effects of the chemical on color reversion.

Throughout the experiments all concentrations of chemicals will be based upon the weight of moisture-free unbleached pulp.

Experimental Part

Characteristics of the Pulps Used

The pulp used for most experiments consisted of unbleached neutral sulphite semichemical pulp cooked to a 70 percent yield. The pulp obtained did not require additional cleaning nor screening and was used as received. The unbleached pulp possesed a brightness of 49.5 percent and yellowness of 68.9 percent both measured on the I.P.C. brightness meter.

In addition,experiments were also ran on a commerically bleached neutral sulphite semichemical pulp that contained a minimum of lignin. This pulp was bleached in a three stage system of chlorination,neutralization and hypochlorite and possesed a brightness of 76.5 percent and a yellowness of 84.1 percent.

Experimental Bleaching Procedure

The experimental procedure for the treatment of the pulp with calcium hypochlorite,for the acidification stage, for the hydrogen peroxide bleaching and for the treatment with sodium borohydride follows:

Bleaching with Calcium Hypochlorite: All experiments with calcium hypochlorite were carried out in polyethylene bags at consistency of 10 percent. The temperature during the bleach was kept at 25±1 C by a theromstatically controlled water bath. Control of the pH level throughout the experiment was accomplished by the addition of enough 10 percent sodium hydroxide solution to maintain the pH level above 9.5. Each bleach was terminated when the amount of residual chlorine was less than 1.0 percent, based on the weight of the moisture-free pulp. The amount of residual chlorine was determined according to the method listed in the TAPPI Monograph Number 10, "The Bleaching of Pulp". The amount of available chlorine in the calcium hypochlorite liquor was determined each day according to TAPPI Standard T-611 m 47.

Acidification Procedure: The acidification of the pulp was carried out for a period of 15 minutes at a consistency of 4.5 percent in glass beakers. The temperature of the acid stage was kept at 65±1 C by a thermostatically controlled water bath. Enough of the respective acid was added at 10 percent strength to adjust the pH of the pulp to between 2.5 and 3.0.

Bleaching Procedure for Hydrogen Peroxide: All experiments with hydrogen peroxide were carried out in polyethylene bags at a consistency of 10 percent with the temperature controlled thermostatically at 85±1 C. An equivalent solution of 0.05 percent magnesium sulphate and 5.0 percent sodium silicate was added at the start to stabilize the hydrogen peroxide. The bleach was allowed to run for a period of 90 minutes whereafter, the liquor was titrated to determine residual hydrogen peroxide.

Sodium Borohydride Bleaching Procedure: The treatment of both the bleached and the unbleached pulp with sodium borohydride was carried out in polyethylene bags at a consistency of 10 percent and at a thermostatically controlled temperature of 35±1 C. After a period of one hour the bleaching liquor was analyzed for residual borohydride to determine the completeness of the reaction.

Yield Determination Procedure: The yield determination for each bleach was based on the hypothetical assumption that during bleaching no loss of yield occurs. That from each bleach a certain proportional part based on the original weight of the pulp was taken and dried at 105 C for a period of 24 hour. The percentage yield was then calculated by dividing the weight of the moisture-free part taken, after drying, by the weight of the part that should be present if no loss had occured.

Formation and Evaluation of Handsheets for Optical Test: All brightness handsheets formed during this experiment were made according to TAPPI Standard T-218 m 48. The brightness handsheets were evaluated by means of the I.P.C. brightness meter. All reading were made with the number one filter (457 mu) for the brightness and number seven filter (606 mu) for yellowness.

Color Reversion Determination: Color reversion was determined before and after treatment of the bleached and unbleached pulp with sodium borohydride by the application of both ultra-violet light and heat. The ultra-violet light treatment was carried out in Fade-o-meter machine for a period of 4,8 and 24 hours. The heat treatment was carried out in a moisture-free oven at 221 F for a period of one hour. Before and after each treatment brightness and yellowness values were taken.

Presenation of Results

The results of bleaching experiments with unbleached neutral sulphite semichemical pulp are shown in Table I. Also, in Table I are the results of sodium borohydride treatment of laboratory bleached pulp produced by experiment number VIII.

The results of the effects which ultra-violet light and heat have on both the unbleached sodium borohydride treated pulp and the laboratory bleached sodium borohydride treated pulp (produced by experiment VIII) are shown in Table II.

The results of the effects which ultra-violet light and heat have on the properties of a commercially bleached sodium borohydride treated pulp are shown in Table III.

Discusion of Results

The following is a discusion of the experimental results shown in Tables I,II, and III.

Reinhardt's Bleaching Procedure: The results of experiments number I,II, and III,Table I,showed which effects Reinhardt's bleaching procedure had on the unbleached neutral sulphite semichemical pulp. Included in experiments II and III are the results of the acid soaking stage after hypochlorite treatment. These results showed that a brightness of over 77 percent was realized and that the effect of an acid soaking stage increased the final brightness further when peroxide was used in the last stage.

Bleaching Experiments with Unbleached Neutral Sulphite Semichemical Pulp: Experiments I to XI covered the determination of a relatively simple method for the bleaching of unbleached neutral sulphite semichemical pulp. Experiment VIII, Table I, produced the pulp with brightness values of over 80 percent and with yields in the 90 percent range based on the weight of the pulp.

Effect of Different Acids on Final Brightness of Bleached Pulp: Results thoughout experiments I to IX, Table I, showed that in most cases hydrochloric acid used before the final peroxide stage was superior to sulfuric acid and made possible higher brightness values.

Effects of Sodium Borohydride on the Bleached Experiment VIII Pulp: The results of experiments X to XIII, Table I, showed that, when sodium borohydride was used in varying quantities as an after-treatment for the bleached pulp, a definite increase in brightness was noted. The use of more than one percent sodium borohydride, seems not to be justified.

Effect of Ultra-Violet Irradiation on Unbleached Pulp and on Bleached Experiment VIII Sodium Borohydride Treated Pulp: The results of experiments O-O to O-III, Table II, showed that sodium borohydride had practically no effect on retarding the color reversion of the unbleached pulp when subjected to ultra-violet irradiation. Experiments V-O to V-III, Table II, showed that sodium borohydride treatment of laboratory bleached pulp (experiment VIII) had no effect on decreasing the reversion properties of the pulp caused by ultra-violet irradiation.

Effects of Heat Treatment on Unbleached and Bleached Experiment VIII Sodium Borohydride Treated Pulp: The results of heat treatment on sodium borohydride treated unbleached and laboratory bleached experiment VIII pulp(experiments O'-O to O'-III and VI'-O to VI'-III,Table II) showed that sodium borohydride had practically no effect on increasing the stability of the pulp which was already relatively stable before sodium borohydride treatment.

Effect of Ultra-Violet Irradiation on a Commercially Bleached Sodium Borohydride Treated Pulp Containing Practically no Lignin: The results of experiments F-O to F-III,Table III, showed that, when a commerically bleached pulp was treated with sodium borohydride the brightness of that pulp was increased further by the sodium borohydride treatment.Upon ultra-violet irradiation, the sodium borohydride treated pulp showed far less loss in brightness (color reversion) than established for the commerically bleached pulp as received,

Effect of Heat Treatment on a Commercially Bleached Sodium Borohydride Treated Pulp Containing Practically no Lignin: The experimental results of experiments F'-O to F'-III,Table III, showed that,when a commerically bleached pulp was treated with sodium borohydride and thereafter,exposed to a temperature of 105 C (221 F) for one hour,the heat stability of the borohydride treated pulp was improved significantly.

Conclusions

From the experimental results shown in Tables I,II and III the following conclusions may be drawn:

1. It was possible to bleach unbleached neutral sulphite semichemical pulp cooked to 70 percent yield to a brightness level above 80 percent by hypochlorite treatment,followed by an acid soaking stage and,finally, by peroxide treatment.
2. The addition of an acid soaking stage after the hypochlorite stage and before the peroxide stage increased the final brightness significantly.
3. Hydrochloric acid,when used in the acid soaking stage, produced a brightness increase which was greater than that produced with sulfuric acid.
4. Sodium borohydride treatment of the unbleached pulp, the bleached lignin-containing pulp and the bleached lignin-free neutral sulphite semichemical pulp produced a definite improvement in brightness.
5. The use of sodium borohydride in quantities greater than one percent gave only limited brightness increase.
6. Sodium borohydride treatment influenced the heat stability (in terms of brightness) favorably in the case of the commerically bleached lignin-free neutral sulphite semichemical pulp but did neither improve the heat stability of the lignin-containing unbleached nor the lignin-containing laboratory bleached neutral sulphite semichemical pulp produced by experiment VIII.

7. The loss of brightness caused by ultra-violet irradiation was substantically reduced by sodium borohydride treatment in the case of the bleached lignin-free pulp. However sodium borohydride treatment did not show any promise as means of increasing color stability under ultra-violet irradiation in the case of the other two lignin-containing pulps.

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BLEACHING EXPERIMENTS WITH N.S.S.C. PULP

Stage	*	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.
1.	Chlorine as Hypo - %	7.5	7.5	7.5	7.5	7.5	10.0	10.0	15.0	15.0	15.0	15.0	15.0	15.0
	Brightness[1]	69.3	69.3	66.8	66.8	66.8	68.0	68.0	79.7	79.7	-	-	-	-
	Yellowness[2]	84.4	84.4	84.2	84.2	84.2	85.3	85.3	85.7	85.7	-	-	-	-
	Yield[3]	95.1	95.1	97.6	97.6	97.6	97.4	97.4	86.9	86.9	-	-	-	-
2.	Chlorine as Hypo - %	3.0	3.0	7.5	7.5	7.5	0	0	0	0	0	0	0	0
	Brightness	71.6	71.6	75.1	75.1	75.1	-	-	-	-	-	-	-	-
	Yellowness	84.7	84.7	85.4	85.4	85.4	-	-	-	-	-	-	-	-
	Yield	92.9	92.9	91.0	91.0	91.0	-	-	-	-	-	-	-	-
3.	Acid Soaking	HCL	H_2SO_4	NO	HCL	H_2SO_4	HCL	H2SO4	HCL	H_2SO_4	HCL	HCL	HCL	HCL
	Brightness	72.4	72.8	73.3	70.9	72.8	67.3	68.2	77.1	77.5	-	-	-	-
	Yellowness	85.0	86.4	86.3	82.5	83.3	85.3	85.7	84.3	85.0	-	-	-	-
	Yield	90.2	89.8	-	-	-	92.9	94.8	84.2	84.7	-	-	-	-
4.	Hydrogen Peroxide - %	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
	Brightness	82.8	80.2	77.6	82.6	81.5	79.8	76.6	86.3	86.2	-	-	-	-
	Yellowness	87.0	86.5	85.5	85.4	85.7	85.8	85.3	87.2	86.8	-	-	-	-
	Yield	88.5	88.0	90.6	90.0	85.0	84.5	80.0	82.8 (4)	83.5	-	-	-	-
5.	Sodium Borohydride - %	-	-	-	-	-	-	-	-	-	0	1.0	2.0	3.0
	Brightness	-	-	-	-	-	-	-	-	-	78.3	82.2	82.4	83.5
	Yellowness	-	-	-	-	-	-	-	-	-	87.3	87.2	87.5	87.7

* - All chemical concentrations are based on the weight of the moisture-free, unbleached pulp.

1. Brightness was measured on the I.P.C. brightness meter at the number one filter.

2. Yellowness was measured on the I.P.C. brightness meter at the number seven filter.

3. The yield was based on the original weight of the moisture-free, unbleached pulp.

4. A control check of this yield showed the actual yield to be 89.3 percent.

Results of treatment of the sodium borohydride pulp with Ultra-violet light and heat, 105 F.

Sample	Initial Bright.	Initial Yellow	Control Bright.[1]	Bright. 4 hr.	Bright. 8 hr.	Bright. 24 hr.	ΔB[2]	Control Yellow	Yellow 4 hr.	Yellow 8 hr	Yellow 24 hr.	ΔY
Bleached, experiment number VIII, pulp treated with sodium borohydride.[3]												
VI-0	79.1	87.1	77.5	62.8	59.0	56.3	22.8	86.0	81.1	80.0	78.2	9.3
VI-1	82.1	87.8	79.9	67.3	62.1	56.5	25.6	86.5	83.5	81.0	79.1	8.7
VI-2	82.0	88.0	80.5	66.4	62.9	58.3	23.7	86.9	82.5	80.9	79.6	8.4
VI-3	83.5	87.1	77.8	66.2	61.4	58.4	25.1	87.0	81.8	79.4	79.4	7.7
Unbleached pulp treated with sodium borohydride												
O-0	51.2	71.9	51.3	48.7	43.2	41.1	10.1	70.5	68.2	67.2	66.9	5.0
O-1	56.0	74.1	56.9	47.6	45.6	43.3	12.7	72.0	68.0	69.0	69.0	5.1
O-2	58.0	75.0	57.6	48.8	45.1	42.0	16.0	73.7	70.2	69.0	69.1	5.9
O-3	58.1	75.0	58.5	49.3	44.5	42.0	16.1	74.5	69.5	69.7	69.4	5.6

Results of heat treatment of pulp treated with sodium borohydride. (Temp. 221 F. Time 1 hour.)

	O′-0		O′-1		O′-2		O′-3	
	Before	After	Before	After	Before	After	Before	After
Brightness at the #1 filter	52.0	51.7	57.7	56.0	58.4	58.2	58.8	58.1
Yellowness at the #7 filter	71.0	71.5	73.2	73.5	73.9	74.1	74.9	74.8

	VI′-0		VI′-1		VI′-2		VI′-3	
	Before	After	Before	After	Before	After	Before	After
Brightness at the #1 filter	78.8	77.8	82.5	80.5	81.9	81.5	83.0	82.4
Yellowness at the #7 filter	87.3	86.5	86.9	87.3	87.7	86.5	87.0	87.1

1. The control brightness and yellowness values are from the effects of the heat only in the Ultra-violet light treatment. (105 F)
2. The ΔB and the ΔY values are the differences between the initial value and the final value.
3. The suffix after the Roman numerical VI and the zero refer to the percent of borohydride used in the treatment.

Table III.

Results of treatment of a Lignin-free pulp with sodium borohydride

Treatment of borohydride pulp with Ultra-violet light and heat at 105 F

Sample	Initial Bright.	Initial Yellow.	Control Bright.[1]	Bright. 4 hr.	Bright 8 hr.	Bright. 24 hr.	Δ B[2]	Control yellow	Yellow 4 hr.	Yellow 8 hr.	Yellow 24 hr.	Δ Y
F-0[3]	78.9	85.4	71.5	68.0	67.0	67.1	11.8	80.6	77.8	77.6	77.0	8.4
F-I	82.2	84.5	76.8	75.0	75.1	75.0	7.2	84.5	81.2	81.2	82.0	2.5
F-II	81.8	84.5	77.0	75.0	75.0	74.2	7.6	84.3	80.8	80.6	80.2	4.1
F-III	82.9	85.8	78.8	72.9	75.3	74.8	8.1	85.8	78.9	80.4	80.2	5.6

Results of treatment of the lignin-free borohydride pulp with heat for a period of one hour at 221 F.

	F-0 Before	F-0 After	F-I Before	F-I After	F-II Before	F-II After	F-III Before	F-III After
Brightness at the #1 filter	76.5	71.3	80.5	77.5	80.8	77.5	80.9	78.5
Yellowness at the #7 filter	85.7	82.8	85.5	85.6	84.8	84.6	85.0	84.5

1. The control brightness and yellowness values are from the effects of the heat only in the ultra-violet light treatment. (105 F)

2. The Δ B and the Δ Y values are differences between the initial value and the final value.

3. The suffix after the letter F refers to the percentages of borohydride used in the treatment.