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The Effects of Acid Pretreatment on Hydrogen Peroxide and Zinc Hydrosulphite Bleached Deinked Magazine Stock

Philip C. Sturman
Western Michigan University

THE EFFECTS OF ACID PRETREATMENT ON HYDROGEN PEROXIDE AND ZINC HYDROSULPHITE BLEACHED DEINKED MAGAZINE STOCK

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PHILIP C. STURMAN

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SCHOOL OF APPLIED ARTS AND SCIENCES

WESTERN MICHIGAN UNIVERSITY

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ABSTRACT

Magazine papers which have a high groundwood content are deinked in large quantities by the deinking mills. For many uses deinked pulp produced from these papers must be bleached. The commonly practiced industrial methods are not wholly satisfactory due to the high shrinkage and lack of brightness stability of the pulp they produce.

In this research project a high groundwood content magazine paper is deinked, washed, and bleached. The following bleaching sequences are applied to portions of the pulp: a single stage hydrogen peroxide treatment, a single stage zinc hydrosulphite treatment, and a two stage hydrogen peroxide-zinc hydrosulphite treatment. In order to determine the effect of acid pretreatment on pulp brightness, portions of the pulp are treated with sulphuric acid and washed before the previously mentioned sequences are applied. It is found that the acid pretreatment does not result in a significant increase in pulp brightness.

A sulphur dioxide post-treatment applied to the bleached pulps increases the brightness values up to 3.0 points.

Yield values for each sequence show that there is little shrinkage due to bleaching.

THE EFFECTS OF ACID PRETREATMENT ON HYDROGEN PEROXIDE AND ZINC HYDROSULPHITE BLEACHED DEINKED MAGAZINE STOCK

LITERATURE SURVEY

INTRODUCTION

In recent years the amount of groundwood in printed magazine paper has increased to a large extent. The present methods of bleaching groundwood containing deinked stock are not fully satisfactory due to the high shrinkage and the lack of stability in brightness of the pulp produced by commonly practiced industrial methods. This literature survey was undertaken to compile information on the methods used in bleaching deinked stock and high lignin containing pulps.

DEFINITIONS

Magazine Papers

Magazine paper may be broadly defined as paper used for periodicals. Specifically, magazine papers are papers which possess good brightness, opacity, and high finish. Of the many grades of coated two-side book papers, magazine papers are relatively low priced grades. The paper should be capable of reproducing standard 120 line screen half-tones when printed either in one color or process work (1). The furnish of the unbleached body stock consists in many cases of approximately fifty per cent groundwood and fifty per cent chemical pulp. Due to the ease of collecting, bundling, and baling

printed magazines, this grade of waste paper is offered in large quantities to paper mills with deinking plants.

Deinking

Deinking is the operation of reducing printed paper to pulp and removing the ink therefrom by mechanical or chemical means (2). Deinked paper stock is manufactured from printed waste paper by a combination of mechanical disintegration, heat, and chemical treatment with caustic soda and/or soda ash. Furthermore, dispersing agents such as sodium tripolyphosphate or tetrasodium pyrophosphate are used to facilitate the removal of ink and extraneous materials such as clay, other fillers, etc. by subsequent washing (2). Since the stock, obtained by treatment with alkali and washing, is low in brightness, it has to be bleached.

BLEACHING OF DEINKED PAPER STOCK

Single Stage Bleaching -- Hypochlorite

Single stage hypochlorite bleaching of deinked paper stock has proven satisfactory in a large number of deinking mills, provided that the groundwood content of the waste paper used does not exceed ten per cent. In order to achieve brightness values up to 75 per cent (as measured by the IPC Brightness Tester), the purchasing of waste paper must be very selective. Also, there is required a relatively large amount of bleach liquor, steam, and an appreciable retention time, which may result in serious degradation of the fiber.

In deinking mills which deink mostly magazine and book papers, the maximum brightness is approximately 70 per cent when hypochlorite is used as the sole bleaching agent.

Bleaching is done both batch-wise and continuously with a definite trend towards the continuous method. Towers are used mostly in the continuous process; however, in some instances, chests are arranged in sequence and used in a continuous fashion. Batch bleaching is done in chests or Bellmers, and it appears that in many cases the equipment used is existing equipment adapted to the bleaching process (3).

Sodium and calcium hypochlorite bleach liquor both are employed; however, calcium hypochlorite is slightly cheaper. The amount of hypochlorite expressed in terms of active chlorine applied to the deinked stock is in general in the range of two to five per cent (based on moisture-free fiber). The quantity of bleach liquor required may vary greatly due to the non-uniformity of the waste paper employed.

In a continuous process where a tower is used, the stock enters the tower at the relatively high consistency of 12 to 15 per cent as compared to the low consistency of three to six per cent that must be employed in batch or continuous processes involving the use of chests.

Retention time for a given operation is dependent upon several factors: the amount of bleach liquor, the consistency, the temperature, and the pH value. Commonly, the stock is at a temperature range of 80 to 120° F, and the hydrogen ion

concentration at the start of the reaction is adjusted to a pH level of nine to ten. Because of this high pH level at the start of the bleaching cycle, the bleached stock leaves the retention vessel in the alkaline state. If the reduction in pH is not adjusted by buffering agents, such as sodium hydroxide or sodium silicate, and the bleaching reaction proceeds from an alkaline to an acid or neutral state in the presence of excess bleach liquor at elevated temperature, the bleaching chemicals will react with the cellulose of the pulp as well as with the lignin. The result is a decreased yield and a loss of desirable papermaking qualities. For best results the reaction is buffered so that the final pH value is 8.0. Hypochlorite bleaching is often followed by sulphur dioxide treatment which results in a gain in brightness, acidification of the stock, and elimination of residual hypochlorite.

After the pulp is bleached, it is common practice to wash the stock to remove water soluble reaction products (3). Kauffman and Martin (4) describe a 100-ton per day mill of this type.

Single Stage Bleaching -- Peroxide

Although there is voluminous literature available on the bleaching of deinked stock, it appears that little has been done in the area of peroxide bleaching of deinked paper stock; there seem to be no pertinent literature references available. However, there were some commercial applications

of deinking with peroxides to yield, after cooking, a deinked stock of higher brightness than produced by use of straight alkalis (5).

Multistage Bleaching -- Chlorination Followed by Hypochlorite Treatment

Chlorination has found increased application in deinking mills because it has become increasingly difficult to produce large quantities of groundwood. To overcome this handicap, chlorination has been adapted by some of the deinking mills. When the groundwood content of the waste paper approaches ten per cent, it is nearly impossible to produce bright and stable pulps by single stage hypochlorite treatment.

The equipment found in multistage bleach plants may vary from chests and Bellmers to towers from discontinued operations, or may have been carefully selected to fit the continuous or semicontinuous process used. In either case the amount of chlorine applied in the first stage is largely dependent upon the amount of groundwood present (3). Whether chlorination takes place in chests, pipe lines (6), or upward-flow chlorination towers, the chlorine gas is bubbled into the low consistency stock at about three per cent, with sufficient agitation to insure thorough mixing of the chemical with the pulp. Reaction time is dependent upon the rate of production in the continuous process and upon individual mill experience in the batch process. After chlorination, the stock is

washed and deckered to a consistency of 12 to 15 per cent for the hypochlorite stage. It appears that three to six per cent available chlorine is employed in the hypochlorite stage with retention times up to four hours at 110° F. Brightness values in the range of 72 to 75 per cent may be produced(3).

Multistage Bleaching -- Chlorination, Caustic Extraction, and Hypochlorite Treatment

In order to produce a stable high-brightness pulp from deinked stock of 20 per cent groundwood content, it was found advantageous to employ a three stage process consisting of chlorination, caustic extraction, and hypochlorite bleaching. With this sequence it was possible to produce high brightness pulps of 76 to 80 per cent brightness consistently. These pulps were almost as stable as good, fully bleached chemical pulps.

In the continuous process, chlorination takes place in an upward-flow chlorination tower. Three to four per cent chlorine is applied to stock at three per cent consistency. The chlorinated pulp leaves the top of the tower after a retention time of 80 to 100 minutes. The stock is diluted with white water preceding washing and thickening to 12 to 14 per cent consistency. One per cent caustic soda and steam are mixed with pulp in a single-shaft mixer, and the pulp is dropped into a downward-flow alkali-resistant tower. The maximum retention time is two hours. A screw conveyor removes

the stock from the tower and conveys it to a dilution chest from which it is pumped to a vacuum washer in order to remove the reaction products. The 12 to 14 per cent consistency stock passes again into a single-shaft mixer where the pulp is mixed with steam and rom two to three per cent available chlorine in the form of hypochlorite. Thereafter, it is dropped into a third tower identical with the caustic extraction tower where the actual whitening of the pulp takes place. The pulp is washed over a vacuum washer. Pulp bleached in such a manner approaches the stability of a good grade of chemical pulp (3).

Since high groundwood-content deinked stock possesses limited brightness stability when bleached by means of hypochlorite, and since this type of deinked stock requires a large quantity of chemicals in multistage bleaching, a survey of bleaching methods used in bleaching groundwood and chemi-mechanical pulps follows.

BLEACHING MECHANICAL AND CHEMI-MECHANICAL PULPS FOR HIGH YIELD

Groundwood and some chemi-mechanical pulps are bleached with hypochlorite, peroxides, or hydrosulphites if one wants to avoid excessive losses in bleaching. The various treatments may be applied in single or multistage processes, depending upon the ultimate use of the pulp (7).

Single Stage bleaching -- Hypochlorite

Hypochlorite bleaching of groundwood is best carried out

in a batch operation. Due to the difficulty involved in controlling the bleaching process at high consistency, groundwood is usually bleached at five to six per cent consistency. The temperature is maintained at 100° F because it is easy to control the reaction at that temperature level. When up to 15 per cent available chlorine is used, brightness gains are readily achieved. Discoloration of the pulp occurs if the pH value of the stock during the bleaching process rises above 11 or falls below 9. Additional chlorine is required to overcome this discoloration. At the end of the bleaching reaction, either before or after washing, the pH level is adjusted to the range of 5.0 to 5.5.

Bleaching of groundwood with hypochlorite is, in many cases, about equal in cost to bleaching it with peroxide. Depending upon the type of pulp and the brightness required, the cost of hypochlorite bleaching per point per ton of pulp lies between $0.80 and $1.00 (8).

Snyder (7) stated that cold soda hardwood pulp could be bleached to a brightness of 70 per cent using 10 per cent chlorine in the form of hypochlorite. However, when a higher brightness was required, the hardwood pulp was mixed with spruce pulp and bleached a second time using peroxide. Cold soda pulp may also be bleached effectively with peroxide, but hydrosulphite was claimed to be ineffective (8).

Single Stage Bleaching -- Peroxide

Peroxide bleaching with either hydrogen peroxide, sodium

peroxide, or a mixture of the two will usually bleach groundwood to a brightness of 58 to 73 per cent in a single stage(9). Barton (10) found that increase in pulp brightness became negligible after the application of three per cent sodium peroxide based upon moisture-free pulp. Generally, an industrial application of two per cent peroxide produces a brightness gain for most pulps in the range of 10 to 12 points (8). Peroxide bleaching may take place at any consistency with efficiency increased as the consistency is increased and may be carried out either as a continuous or batch operation (8). At medium consistency, 12 to 15 per cent, and a temperature of 110 to 115° F the retention time is approximately one and a half to two hours (11). For optimum brightness gain the pH value of the stock after the bleach has been added should be between 10.0 and 10.5. The cost per point brightness gain expressed in tons of pulp is between $0.70 and $1.00, depending upon the brightness of the pulp desired. At the end of the bleaching cycle the residual peroxide is usually neutralized with sulphur dioxide (8).

Single Stage Bleaching -- Hydrosulphite

Zinc hydrosulphite has been used for bleaching groundwood for many years. Industrial bleaching usually takes place at low consistencies of four to six per cent since it is harder to obtain good mixing of the chemical with the pulp at higher consistencies without mixing in some air, which

decomposes the hydrosulphite. Bleaching usually takes place at a pH level between five and five and a half, since at higher pH levels there is yellowing of the stock. At a pH of four and a half or lower the hydrosulphite will be decomposed. Rapid mixing of the pulp and hydrosulphite, retention time with as little air as possible being introduced into the pulp, and a relatively high temperature are the most important features of a hydrosulphite bleaching treatment. Temperatures in the range of 90 to 160° F are common. Most of the brightness increase, about 90 per cent, is obtained in one hour at 90° F, and the completion of the reaction takes three to four hours. At 160° F, 90 per cent of the brightness is obtained in 15 minutes with completion of the reaction in one hour. Temperature also affects the final brightness. With each increase of 20° F the final brightness may be increased one point. Brightness gains of eight to ten points are possible for pulps produced from most woods, if one uses one per cent hydrosulphite. The chemical cost for each point of brightness increase per ton of pulp is dependent upon the brightness desired and also upon the type of wood used; it is usually between $0.30 and $0.60. The residual hydrosulphite is decomposed automatically in the machine chest when it comes in contact with air (8).

Multistage Bleaching -- Peroxide and Hydrosulphite

In order to obtain higher brightness levels than those possible with either peroxide or hydrosulphite, the two

chemicals may be used in sequence. With these two stages, brightness values over 80 per cent may be obtained (8). Barton (10) found that aspen groundwood could be bleached with 2.2 per cent sodium peroxide and 1.0 per cent hydrosulphite to a brightness of 82 per cent. Bauer (12) found that cold caustic soda pulp could be bleached in industrial application to a brightness in the range of 74 to 76 per cent, provided that the peroxide stage was preceded by a pH adjustment to about 2.5 to 3.0 and followed by washing. In each of the above cases sulphur dioxide was used to neutralize the excess peroxide before the hydrosulphite stage. The cost of chemicals for bleaching cold soda pulp to a brightness level of 74 to 76 per cent was about $20.10 per ton of air-dried pulp, when a two stage process using two per cent sodium peroxide and a one per cent hydrosulphite was employed (12).

CONCLUSION

Since the literature survey revealed little information concerning either peroxide or hydrosulphite or combinations of the two in bleaching deinked stock, it was decided to explore the use of peroxide and zinc hydrosulphite, which have been found to be useful in bleaching some chemi-mechanical pulps (12).

EXPERIMENTAL DESIGN

It was the objective of this thesis to determine a method of bleaching high groundwood-content deinked magazine stock to adequate brightness without large shrinkage. Deinked stock prepared from the filler pages of "Life" magazine was used. Peroxide, hydrosulphite, and combinations of both chemicals were used as bleaching agents.

The thoroughly washed deinked pulp was divided into two distinct types identified as "N" — which denotes normal and "A" — which means acidified and washed. Both the normal and the acidified deinked stock were used in two series of parallel experiments.

The deinked stock, both "N" and "A" types, was bleached by means of a multistage sequence consisting of a peroxide stage followed by a hydrosulphite treatment. After each stage the pulp was thoroughly washed. For a separate but similar set of experiments sulphur dioxide dissolved in water was used as a substitute for the plain distilled wash water after the hydrosulphite stage and single stage hydrogen peroxide. Comparisons of optical tests performed on handsheets prepared from each set of bleached pulps showed the effect of the different bleaching methods.

Single stage peroxide treatment and single stage hydrosulphite treatment were also applied to the two types of deinked magazine stock in order to show the contribution which each chemical made to the two-stage bleaching experiment.

DESCRIPTION OF EXPERIMENTAL TECHNIQUES

PREPARATION OF DEINKED MAGAZINE STOCK

Batches of 200 g. of "Life" magazine paper were cooked with four per cent caustic soda, based on moisture-free fiber, at a temperature of 165° F, for 45 minutes. Cooking took place at a consistency of four per cent. After attaining a temperature of 165° F, defibering was performed on a drill press equipped with a blunt-edged agitator and running at medium speed.

A laboratory side-hill washer, built by Kalamazoo Tank and Silo Company, was used to wash the cooked and defibered stock. The angle of the screen was 43 degrees and the screen mesh was 0.075 in. The stock was washed six times using the following procedure. After emptying two trays of stock onto the screen, approximately one-half of the stock was deckered from the bottom of the washer by hand, diluted to about 1.5 per cent consistency, and emptied again over the screen. The preceding operations were repeated until each batch of stock was washed six times.

ACIDIFICATION

The deinked magazine stock was thoroughly mixed to obtain uniformity and divided into two separate batches. One batch was labeled "N" — normal deinked stock — and set aside for the bleaching experiments.

The pH of the other batch was adjusted with dilute sulphuric acid to between 2.5 and 3.0 and allowed to stand for at least one hour. A Buchner funnel fitted with Whatman No. 2 filter paper was used to wash and dewater the stock without the loss of fines. Demineralized water was used to wash the acidified pulp. The acid-pretreated deinked stock was designated "A" — which denotes acidified and washed.

HYDROGEN PEROXIDE BLEACHING

A bleach liquor was prepared containing the following percentages of chemicals, based on the moisture-free weight of the pulp:

1. 0.05 per cent Epsom salt
2. 5.00 per cent silicate of soda
3. 2.50 per cent hydrogen peroxide
4. 1.55 per cent caustic soda

Using 30 g. of moisture-free pulp per bleaching experiment, the proper amount of chemicals were dissolved in a 250-ml. volumetric flask so that 25-ml. aliquot portions could be accurately delivered to the pulp.

Hydrogen peroxide bleaching was performed in polyethylene bags. After the pulp was weighed into the bag and the bleach liquor was added, a calculated amount of hot water was added to bring the temperature of the material in the bag to approximately 155° F and to adjust the consistency to 10 per cent.

The bag was next placed in a constant temperature water bath at 155° F for 90 minutes.

At the end of the bleaching time, a 25-ml. portion of the liquid squeezed from the pulp was titrated with 0.1 N sodium thiosulphate to determine the amount of hydrogen peroxide left. The residual hydrogen peroxide was calculated using equasion (1) in the Appendix. Residuals are expressed in terms of per cent of 50 per cent hydrogen peroxide applied.

ZINC HYDROSULPHITE BLEACHING

Zinc hydrosulphite bleaching was performed in 1000-ml. Erlenmyer flasks. A calculated amount of preboiled hot water was added to the 30 g. of pulp to raise the temperature to 155° F and to decrease the consistency to four per cent.

It was assumed that there was no loss in the pulp bleached by the hydrogen peroxide and that the consistency of the pulp after washing and dewatering on the Buchner funnel was 25 per cent. Based on these assumptions, the hydrogen peroxide bleached pulp was prepared for the zinc hydrosulphite treatment.

Based on the moisture-free weight of the pulp, 0.8 per cent trisodium phosphate and 1.2 per cent zinc hydrosulphite were carefully stirred into the pulp. The trisodium phosphate was added before the zinc hydrosulphite to act as a stabilizing agent. After the zinc hydrosulphite was added to the pulp, the pH was adjusted to between 5.0 and 5.5.

YIELD DETERMINATION

All bleaching experiments were performed in duplicate. The duplicate was used for yield determinations. A pad was made of the bleached pulp on a Buchner funnel fitted with Whatman No. 2 filter paper. The filter paper was removed from the pad before the pad was placed in a constant temperature oven at 105° C. After a constant weight was attained, the per cent yield was determined for the pulp by dividing the weight of the pad by the original weight of the pulp and multiplying the result by one hundred.

WASHING

All washing was done on a Buchner funnel fitted with Whatman No. 2 filter paper. At the end of a bleaching treatment, the pulp was washed with either four liters of demineralized water or demineralized water containing dissolved sulphur dioxide. The pH of the sulphur dioxide water was in the range of 2.5 to 3.0

OPTICAL HANDSHEETS

A portion of the pulp corresponding approximately to five grams moisture-free fiber was withdrawn, diluted to two liters, and cleared in a TAPPI disintegrator for five minutes. Two brightness sheets were formed on a Buchner funnel, pressed and dried according to TAPPI Standard T 217 m-48.

DETERMINATION OF BRIGHTNESS

Brightness values were determined on an Institute of Paper Chemistry Brightness Tester at an average effective wavelength of 457 millimicrons. 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 a No. 7 filter. Yellowness is a measure of the pulp's reflectance in the yellow region of the spectrum.

EXPERIMENTS PERFORMED

The bleaching sequences performed on the normal and acidified pulps are listed below. The number preceding each sequence is used in the tables and graphs to identify the type of pulp and treatments it has undergone.

Normal Deinked Stock

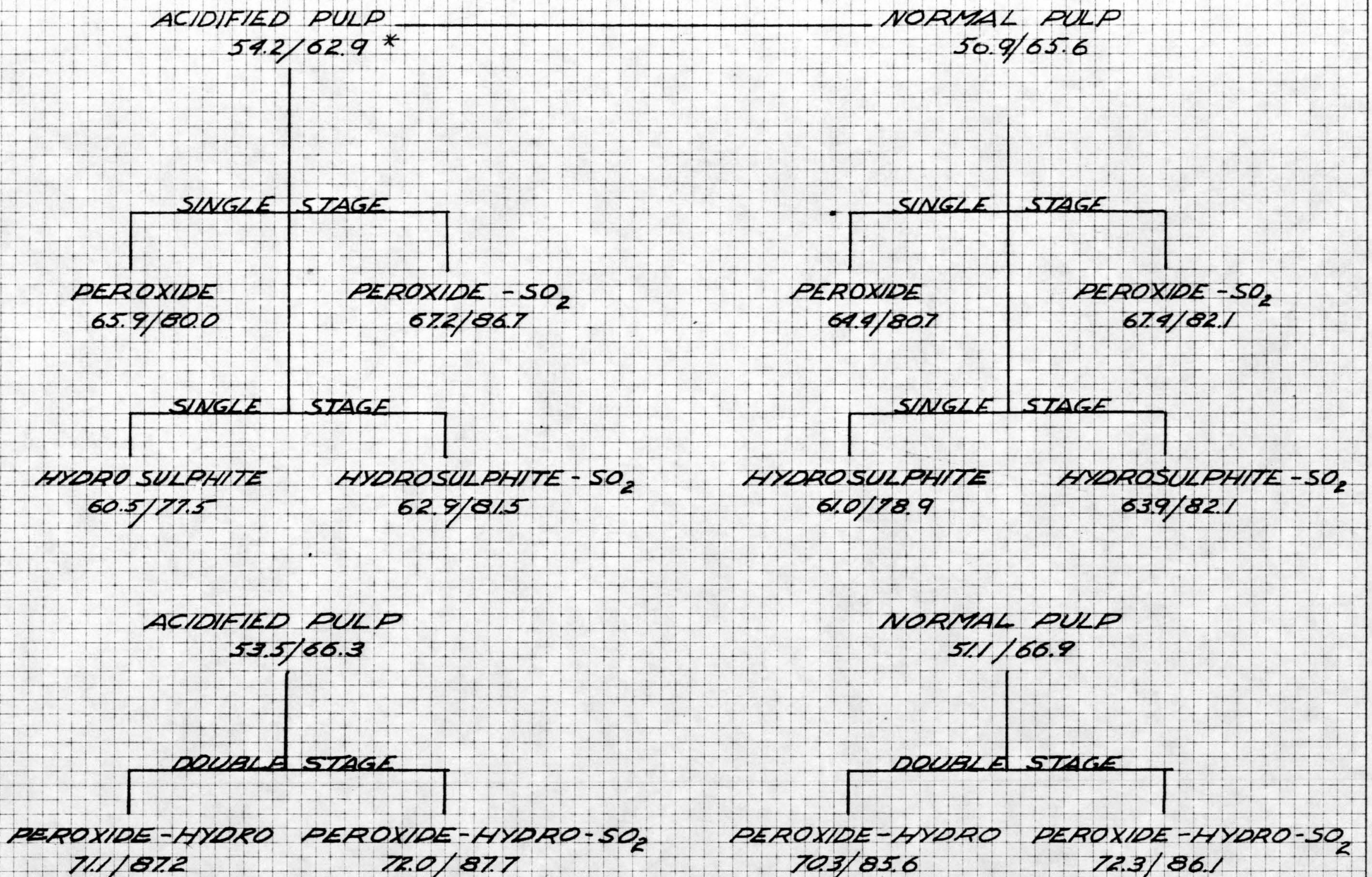
1. Single stage hydrogen peroxide
2. Single stage hydrogen peroxide with a sulphur dioxide posttreatment
3. Single stage zinc hydrosulphite
4. Single stage zinc hydrosulphite with a sulphur dioxide posttreatment
5. Double stage; hydrogen peroxide-zinc hydrosulphite
6. Double stage; hydrogen peroxide-zinc hydrosulphite with a sulphur dioxide posttreatment

Acidified Deinked Stock

7. Single stage hydrogen peroxide
8. Single stage hydrogen peroxide with a sulphur dioxide posttreatment
9. Single stage zinc hydrosulphite
10. Single stage zinc hydrosulphite with a sulphur dioxide posttreatment
11. Double stage; hydrogen peroxide-zinc hydrosulphite
12. Double stage; hydrogen peroxide-zinc hydrosulphite with a sulphur dioxide posttreatment

The significance of each experiment may be seen from Diagram I. On one side of the diagram is shown the sequences applied to the acidified pulp and on the other side, the sequences applied to the normal pulp. Similar treatments applied to the two types of pulps are directly across from each other and occupy the same relative position in both schematic drawings. The manner in which the sequences are arranged facilitates comparisons. Comparisons may easily be made

DIAGRAM I BLEACHING SEQUENCES APPLIED TO PULPS



* BRIGHTNESS / YELLOWNESS = 54.2/62.9

between two types of pulps with identical treatments. Also, the effects of a sulphur dioxide treatment applies to similarly bleached pulps may be evaluated by subtracting the optical test values of the pulp without a sulphur dioxide treatment from the one with a sulphur dioxide treatment. As indicated above, the pulp without a sulphur dioxide treatment is the control used to evaluate the results of the sulphur dioxide treatment. Other comparisons are made in a similar manner.

PRESENTATION OF RESULTS

The results of the effects of single stage and two stage bleaching with hydrogen peroxide and/or zinc hydrosulphite are shown in Tables I and II respectively and presented in the form of bar graphs in Figure 1 and Figure 2. Shown graphically in Figure 1 and Figure 2 are also the results obtained from two stage bleaching. Yield values obtained for the various bleaching sequences are given in Table III.

TABLE I

SINGLE STAGE BLEACHING

Identification +	% H_2O_2 (50%) based on M.F. wt. of pulp	Residual % H_2O_2 (50%) applied	Brightness 457 millimicrons	Yellowness 606 millimicrons
0	----	----	50.9	65.6
1	2.5	31.0	64.4	80.7
2	2.5	24.6	67.4	82.1
3*	----	----	61.0	78.7
4*	----	----	63.9	82.1
0-0	----	----	54.2	67.9
7	2.5	22.2	65.9	85.0
8	2.5	22.2	67.2	86.7
9*	----	----	60.5	77.5
10*	----	----	62.9	81.5

*1.2% zinc hydrosulphite, based on M.F. pulp was used. The residual was not determined at the end of the bleaching time.

+See page 18./9

TABLE II

DOUBLE STAGE BLEACHING

Normal Deinked Stock

Identification+	% H_2O_2 (50%) based on M.F. wt. of pulp	Residual % H_2O_2 (50%) applied	Brightness 457 millimicrons	Yellowness 606 millimicrons
0'	----	----	51.1	66.9
5*	2.5	35.5	70.3	72.3
6*	2.5	35.5	72.3	86.1

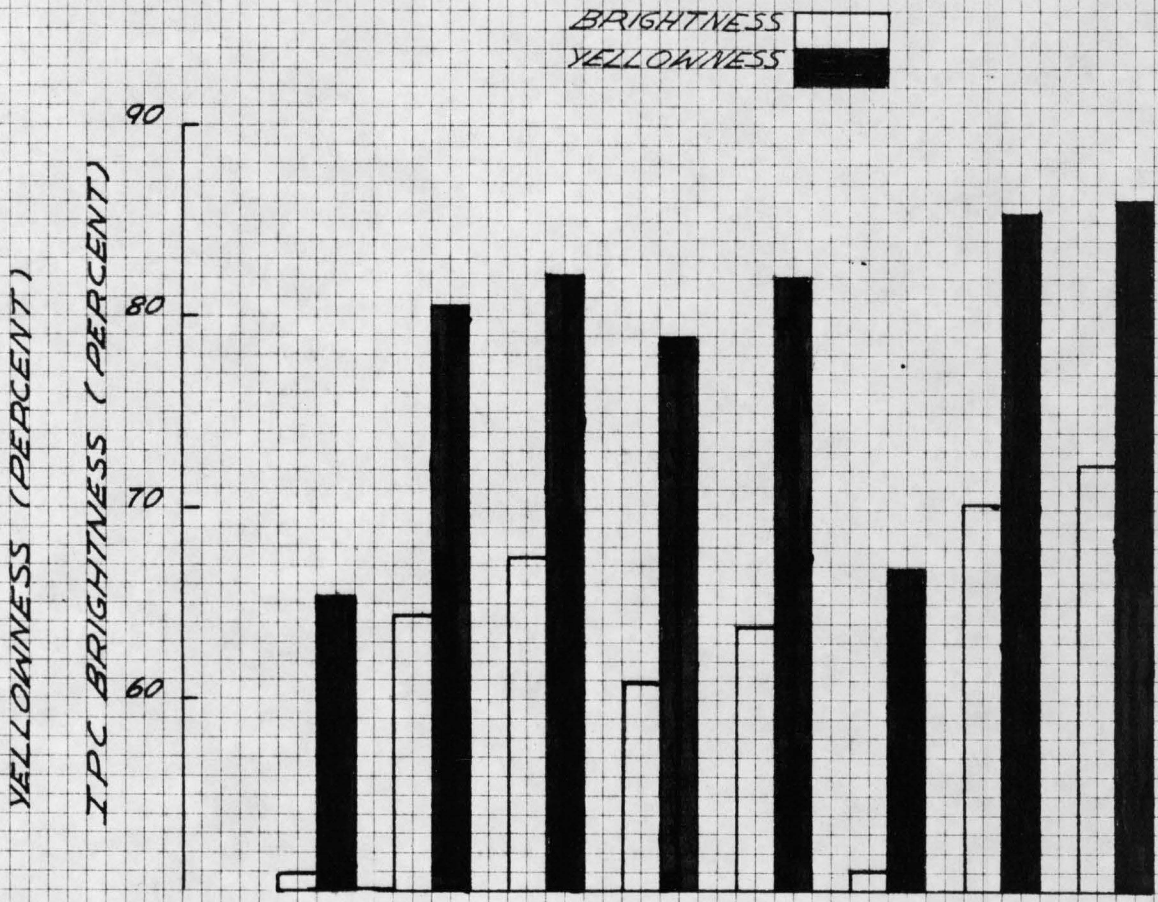
Acidified Deinked Stock

Identification+	% H_2O_2 (50%) based on M.F. wt. of pulp	Residual % H_2O_2 (50%) applied	Brightness 457 millimicrons	Yellowness 606 millimicrons
0'-0	----	----	53.5	66.3
11*	2.5	35.5	71.1	87.2
12*	2.5	33.7	72.0	87.7

*1.2% zinc hydrosulphite, based on the M.F. pulp was applied. The residual was not determined at the end of the bleaching time.

+See page ~~18~~. 19

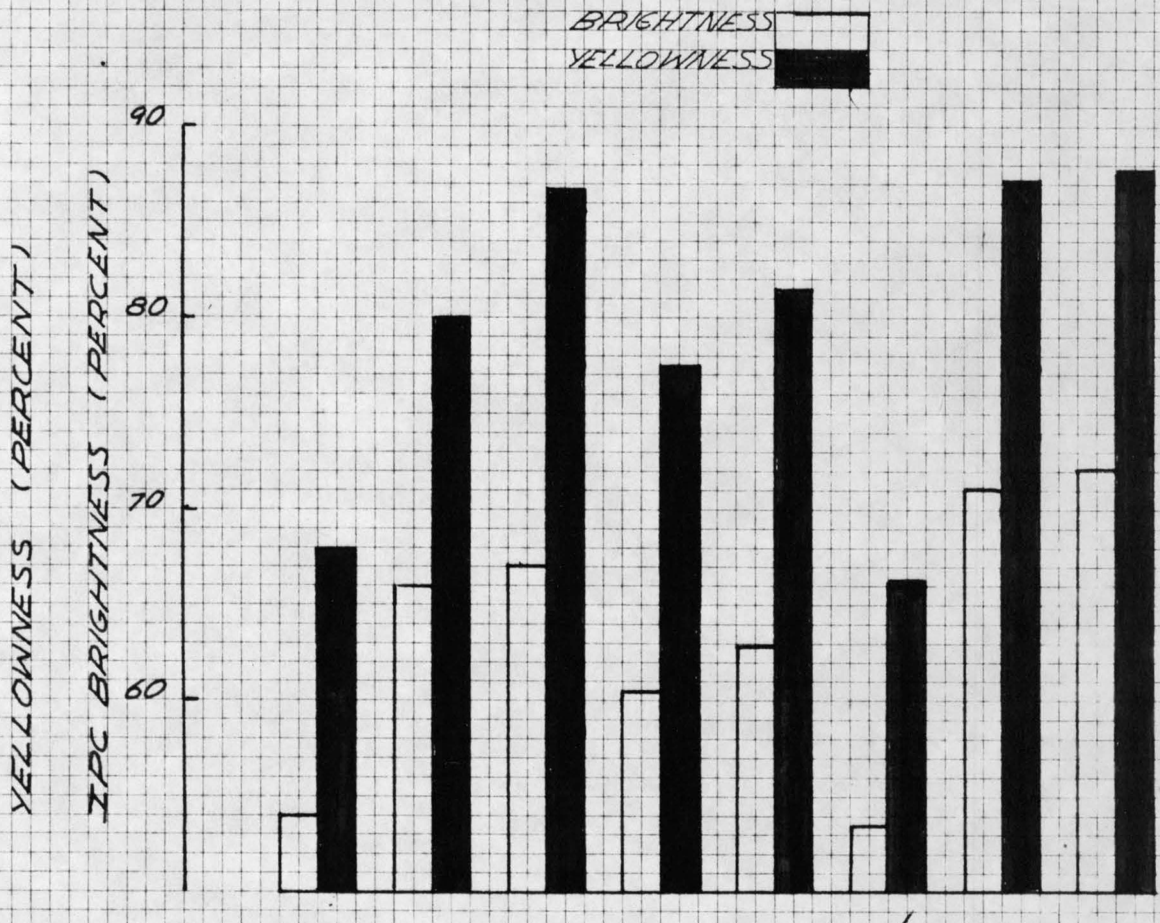
FIG. 1 THE EFFECT OF PEROXIDE AND/OR HYDROSULPHITE ON THE NORMAL PULP



IDENTIFICATION		0*	1	2	3	4	0′	5	6
ACIDIFICATION		NO	NO	NO	NO	NO	NO	NO	NO
H_2O_2 (50%)	%	NO	2.5	2.5	NO	NO	NO	2.5	2.5
ZnS_2O_4	%	NO	NO	NO	1.2	1.2	NO	1.2	1.2
SO_2 TREATMENT		NO	NO	YES	NO	YES	NO	NO	YES
YIELD	%	—	100.0	97.7	100.0	98.7	—	99.0	98.7

* 0 AND 0′ DENOTE UNBLEACHED PULP

FIG. 2 THE EFFECT OF PEROXIDE AND/OR HYDROSULPHITE ON THE ACIDIFIED PULP



IDENTIFICATION		0-0	7	8	9	10	0'-0	11	12
ACIDIFICATION		YES	YES	YES	YES	YES	YES	YES	YES
H_2O_2 (50%)	%	NO	2.5	2.5	NO	NO	NO	2.5	2.5
ZnS_2O_4	%	NO	NO	NO	1.2	1.2	NO	1.2	1.2
SO_2 TREATMENT		NO	NO	YES	NO	YES	NO	NO	YES
YIELD	%	—	100.0	100.0	103.3	99.9	—	99.0	98.7

* 0-0 AND 0'-0 DENOTE UNBLEACHED ACIDIFIED PULP

TABLE III

RESULTS OF YIELD DETERMINATIONS FOR THE BLEACHED PULP

Identification	% Yield
1	100.0
2	97.6
3	100.0
4	98.7
5	99.0
6	98.7
7	100.0
8	100.0
9	103.3
10	99.9
11	99.0
12	98.7

DISCUSSION OF RESULTS

Comparisons were made between two types of pulp: "normal" and "acidified." "Normal" designates the pulp which was deinked but received no acid treatment prior to bleaching. "Acidified" designates the pulp which was pretreated with dilute sulphuric acid.

The normal pulp was treated with sulphuric acid to yield the type of pulp designated as acidified. Accompanying the treatment of the pulp with sulphuric acid was an average brightness increase of 2.9 points.

Comparison of the brightness and yellowness values of the acidified pulps and the normal pulps indicates that the acid pretreatment was beneficial for the pulps bleached with either a single stage hydrogen peroxide or a double stage hydrogen peroxide-zinc hydrosulphite treatment. For all other treatments there were no advantages to be gained by the pretreatment.

The brightness value obtained from the acidified pulp bleached with a single stage hydrogen peroxide treatment was 1.5 points higher than that obtained for the normal pulp. However, the hydrogen peroxide residual for the acidified pulp was 22.1 per cent (of the amount applied), as compared with the 31.0 per cent for the normal pulp. This indicates that the small brightness increase of 1.5 points may have been due to the higher peroxide consumption and not to the acid pretreatment.

In the case of the two stage treatment, the brightness value obtained for the acidified pulp was 0.8 points greater than the value obtained for normal pulp. This is not a significant improvement. The yellowness value for the normal pulp was 72.3 per cent as compared to the 87.2 per cent for the acidified pulp, a difference of 14.9 points. Based on these results, it was decided that the normal pulp was the better of the two pulps.

When a sulphur dioxide post-treatment was applied to the two types of pulp bleached by either of the two sequences mentioned above, the normal pulp had a higher brightness than the acidified pulp. For the single stage hydrogen peroxide treatment the normal pulp was 0.2 points brighter than the acidified pulp after the post-treatment with sulphur dioxide. The acidified pulp bleached by a combination of hydrogen peroxide and zinc hydrosulphite was 0.8 points brighter than the normal pulp before the sulphur dioxide post-treatment; it was 0.3 points lower than the normal pulp after the sulphur dioxide treatment.

A sulphur dioxide post-treatment applied to the pulps bleached with hydrogen peroxide, zinc hydrosulphite, or a combination of the two chemicals resulted in an increase in pulp brightness of 0.9 to 3.0 points. The best results, however, were obtained with the normal pulp; the brightness here increased between two and three points. Accompanying

the increase in brightness was also an increase in yellowness for both types of pulp. For the acidified pulps the increases were from 0.5 to 6.7 points. There were smaller increases in yellowness for the normal pulps; these ranged from 0.5 to 3.2 points.

Yield values tabulated in Table III show that there was very little loss in pulp weight due to bleaching with hydrogen peroxide, zinc hydrosulphite, or a combination of the two chemicals. Values obtained ranged from 97.6 to 103.3 per cent of the weight of the unbleached fiber. However, the majority of the values were close to 100 per cent. These high yields may be attributed to several factors. The first is that the pulp used in the bleaching experiments had been processed previously and therefore had few of the naturally occurring soluble materials present in virgin pulp; hence, its yield should be high. Secondly, peroxide has little effect on cellulose, and consequently even the yields with 100 per cent groundwood are normally 98 to 102 per cent of the weight of the unbleached pulp -- part of the yield being derived from the bleaching residuals left in the pulp (13). Thirdly, zinc hydrosulphite is believed to act as a reducing agent, adding hydrogen to the unsaturation in chromophoric groups in the colored constituents, thus reducing them to a colorless form. It follows from this that the addition of the hydrogen to the pulp would increase its weight slightly.

CONCLUSIONS

The experiments performed on the high-groundwood-content deinked magazine stock indicate that:

1. Pretreatment with sulphuric acid prior to bleaching with hydrogen peroxide, zinc hydrosulphite, or a combination of the two chemicals does not result in an increase in pulp brightness greater than that which may be obtained without the pretreatment.

2. A sulphur dioxide post-treatment applied to the bleached pulps produces an increase in brightness.

3. There is little or no loss in the weight of the pulps bleached with hydrogen peroxide, zinc hydrosulphite, or a combination of the two chemicals.

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APPENDIX

DETERMINATION OF HYDROGEN PEROXIDE RESIDUAL

1. Mix: 10 ml. sulphuric acid (25%)
   1 ml. potassium iodide (10%)
   1 to 2 drops ammonium molybdate (10%)

2. Titrate with 0.1 N thiosulphate, using soluble starch near the end point as an indicator. The color change is from blue to clear.

3. Calculation of per cent hydrogen peroxide residual:

$$\% \; H_2O_2 \text{ Residual}^* = \frac{x\,(100-D)\;t\;(100)}{D\;(\%\;H_2O_2 \text{ applied})} \qquad \text{eq. (1)}$$

D = % O.D. density of pulp before filtering

t = ml. of 0.1 N sodium thiosulphate used to titrate 25 ml. of filtrate

x = 0.01360 for hydrogen peroxide (50%)

*Expressed in % of H_2O_2 (50%) applied

STANDARDIZATION OF HYDROGEN PEROXIDE

1. Dilute 10 ml. of hydrogen peroxide to 100 ml. with distilled water.

2. Pipet 2 ml. of the diluted peroxide solution into a flask containing 125 ml. of cold 10% sulphuric acid.

3. Add 3 to 4 drops of manganese sulphate solution.

4. Titrate with 0.1 N potassium permanganate to a pink end point.

5. Calculations:

$$\text{ml. } KMnO_4 \times 0.0017 \times 5000 = \text{g. } H_2O_2 \text{ per liter} \qquad \text{eq. (2)}$$