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Two Stage Peroxide-Borohydride Bleaching of Cold Soda Pulp

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TWO STAGE PEROXIDE - BOROHYDRIDE BLEACHING OF COLD SODA PULP

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TABLE OF CONTENTS

SURVEY OF LITERATURE

Introduction

Since the development of cold soda pulping in the early 1950's, the search for suitable bleaching methods has been of primary concern. Cold soda pulp is dark brown in color and resists the bleaching action of most chemicals. Marton (1) suggests that this brown discoloration of hardwood cold soda pulp is due to a material in the cells of the wood, primarily in the heartwood. These substances, which have not been identified, are not the same as lignin but probably develop in a similar manner.

The chemicals most often used in bleaching hardwood cold soda pulps have been peroxides, hypochlorites, hydrosulfites, and most recently borohydrides. A satisfactory bleaching procedure should meet the following objectives:

1. Development of high brightness
2. Retention of the initial high yield
3. Low cost.

In order to achieve these objectives Giertz (2) states that the pulping process should be performed in such a manner that colored lignins do not form and that the bleaching agent should destroy only the coloring material and not react with the lignin. These requirements would eliminate all chlorine compounds which form colored lignin complexes as bleaching agents.

BLEACHING COLD SODA PULP WITH PEROXIDES

The Chemistry of Peroxides

According to Reichert (3), peroxide bleaching is the result of the dissociation of the peroxide molecule.

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

The HO_2^- ion is considered to be the active bleaching agent. Little more is known as to what takes place between this ion and the wood pulp. Some researchers believe that the peroxide selectively oxidizes the coloring matter because the lignin and cellulose undergo no significant change.

The Variables of Peroxide Bleaching

There are primarily three variables in peroxide bleaching —— time, temperature, and the quantity of chemicals used. Foderaro et. al. (4) report that use of a high temperature, which also indicates a low reaction time, is justifiable.

Procedures of Peroxide Bleaching

McEwen (5) obtained a brightness of 70% G.E. by applying 2.0% hydrogen peroxide to an aspen cold soda pulp (original brightness of 50% G.E.) in a high density steep bleach process.

Foderaro et. al. (4) obtained a maximum brightness of 66.9% G.E. by bleaching aspen cold soda pulp (original brightness of 48.8% G.E.) according to the following conditions:

Consistency = 13%

Temperature = 165° F

Percent Hydrogen Peroxide = 0.96%

Percent Sodium Hydroxide = 0.81%

By lowering the temperature to 131° F and increasing the percent sodium hydroxide to 1.16%, they achieved a brightness of 65.5% G.E.

In a report by Coe and Crosby (6) which investigated the effects of various bleaching agents upon a black birch high yield pulp which was similar to cold soda, a brightness gain of 17 G.E. points was obtained by using 2% hydrogen peroxide, 0.05% epsom salts, 5.0% sodium silicate, and 1.3% sodium hydroxide at 85° C for 1.75 hours.

Departing from the conventional bleaching methods, Jahne and Price (7) propose that the cold soda hardwood chips be bleached as they enter the primary double-disk refiner. A brightness of 60% G.E. was obtained from an original brightness of 42% by adding 2.5% hydrogen peroxide, 5.0% sodium silicate, and 0.47% sodium hydroxide and retaining the chips for a maximum time of 4 hours in the secondary refiner. Using the same chemicals under ordinary conditions a brightness of 58% G.E. was produced.

Cold soda pulp made from beech, birch, and maple is being bleached from 45 to 80% G.E. brightness at Gould Paper Co., Lyons Falls, New York according to Fennell, Smedberg, and Stalter (8). A two stage peroxide - hydrosulfite process is used. The unbleached pulp is subjected to a preacidification step using sulfuric acid to reach a pH of 2.5. The hydrogen tower bleaching is carried out at 12% consistency for 2 hours at 170° F. After washing, dilution, and neutralization, sodium hydorsulfite is mixed in and allowed to react at 140° F for 1 hour.

In addition Fennell et. al. (8) report similar bleaching experiments by the DuPont Laboratories. Using a 1.2% hydrogen peroxide stage followed by a 1% sodium hydrosulfite stage, a brightness of 77.1% G.E. was obtained with beech, birch, and maple cold soda (original brightness of 46%), 71.2% for a 50-50 mixture of southern red oak and mixed hardwoods (original brightness of 43%), and 70.5 for aspen (original brightness of 47%).

BLEACHING COLD SODA PULP WITH SODIUM BOROHYDRIDE

The Chemistry of Borohydrides

Jullander and Brune (9) state that borohydrides are strong reducing agents which will reduce water to hydrogen.

$$NaBH_4 + 2H_2O \rightleftharpoons NaBO_2 + 4H_2$$

Varsheney and Lumer (10) present the following decomposition reaction for borohydride in an acid medium:

$$BH_4^- + H_3O^+ + 2H_2O \rightleftharpoons 4H_2 + B(OH)_3$$

In 0.1 N sodium hydroxide only 5% decomposition occurs in 48 hours.

According to Lumer (11), carbonyl groups have been shown to be involved in a number of bleaching reactions. Since sodium borohydride selectively reduces carbonyl groups, this reaction may be related to brightness. In a later report Lumer and co-worker Supka (12) indicated that the polysaccharides contain carbonyl groups which are formed during alkaline degradation and that these consume sodium borohydride during bleaching. In Lumer's work with Varsheney (10) the following equation is given for the stoichiometry

of the reaction:

$$4\ R_2C{=}O + BH_4^- + 2H_2O \rightleftharpoons 4\ R_2CHOH + BO_2^-$$

Although the reduction of carbonyl groups and brightness may be related, Luner and Supka (12) state that it is the reduction of lignin and extractives which results in an increase in brightness.

The presence of some heavy salt ions may influence the effects of sodium borohydride bleaching. Jullander and Brune (9) report that salts of lithium, calcium, barium, and magnesium increase its efficiency, while zinc, cadmium, and aluminum salts have a negative effect. Varsheney and Luner (10) confirmed the hindering effect of foreign ions on borohydride when they found that bleaching with sodium borohydride produced a gray pulp unless the pulp was pre-washed with hydrochloric acid. It was thought that the hydrochloric acid removed metallic ions which formed insoluble borides on reduction.

Procedures of Sodium Borohydride Bleaching

Using 2% sodium borohydride at 35° C, 5% pulp consistency and a pH of 9.4, Mayer and Donofrio (13) obtained a 10.4 G.E. brightness increment on a mechanical pulp. The same effects could be achieved with sodium peroxide but the sodium borohydride pulp possessed distinct advantages in reflectance in the 300 to 425 mμ range.

Luner (11) found that the most effective conditions for bleaching cold soda pulp with sodium borohydride are a high consistency between 10 and 20%, relatively high temperatures between 50 and 75° C, and the use of suspensions which contain 0.4% sodium hydroxide.

Under these conditions he bleached a white birch cold soda pulp with an initial Hunter brightness of45% to 74% using a large excess of sodium borohydride. Luner also found that the brightness increases rapidly followed by a slower increase in brightness.

In a later report by Luner and Supka (12) a white birch cold soda pulp was bleached with sodium borohydride. A maximum brightness increment of 23.0 points was achieved by applying two stages of sodium borohydride to pulp at 15% consistency for 3.75 hours and 2.0 hours, respectively, at 75° C. The second stage was responsible for 6.7 points increase in brightness. The final Hunter brightness of the pulp was 67.6. By lowering the consistency of the pulp to 10%, allowing the first stage to proceed for 6.0 hours, and allowing the second stage to proceed for 7.0 hours, a total increase of 21.2 points was reached.

Luner (11) also proposed to add sodium borohydride to the wood chips during the pulping reaction. This proposal was based on the fact that sodium borohydride is stable under alkaline conditions and that the dark color of cold soda pulp results from alkaline treatment. When white birch chips were soaked for 10 minutes in a range of sodium hydroxide and sodium borohydride concentrations and then refined, it was found that a maximum Hunter brightness of 62.9 was produced from a pulp of 42.8 initial brightness.

Procedures for Bleaching Cold Soda Pulp with Hypochlorites

Brown and Monsson (14) increased the brightness of a cold soda pulp made by a hydrostatic pressure treatment of 1 hour from 49.3

to 73.9% G.E. brightness. 11% chlorine was applied as calcium hypochlorite in a one stage bleach. 3% sodium hydroxide and 4% sodium silicate were added for pH control. The yield based on the unbleached pulp was 95.7%. A study of the physical properties of the bleached pulp showed that the strength was not changed by bleaching.

Coe and Crosby (6) also achieved a good brightness gain with hypochlorite. For a black birch high yield pulp a brightness gain of 30 G.E. points was obtained by applying 10% sodium hypochlorite and 1.3% sodium hydroxide for 1.25 hours at 32° C.

Procedures for Bleaching Cold Soda Pulp with Hydrosulfites

In their study of various bleaching agents Coe and Crosby (6) state that a brightness gain of 7 G.E. points may be achieved by reacting 1% sodium hydrosulfite, 0.5% sulfur dioxide, and a trace of sodium tri-polyphosphate with an unbleached black birch high yield pulp for 0.75 hours at 66° C.

Procedures for Bleaching Cold Soda Pulp with Chlorine Dioxide

Coe and Crosby (6) obtained a brightness gain of 13 G.E. points on a black birch pulp by reacting 10% chlorine dioxide for 4 hours at 62° C.

Bleaching Cold Soda Pulp with Activated Chlorate

In a recent report Marpillero (15) indicates that a cold soda pulp can be bleached to 85% G.E. brightness. Treatment of a cold

soda pulp with activated chlorate gave a 70% overall yield of semibleached, semichemical pulp. This brightness was then increased to 70% by a hypochlorite treatment. Further treatment with activated chlorate raised the brightness to 85%.

Rapson (16), during an analysis of Marpillero's work, found by spectroscopic analysis that activated chlorate contained 0.18% vanadium and 0.16% molybdenum. A synthetic mixture of pure sodium chlorate and vanadium pentoxide gave similar results to those obtained by Marpillero. Rapson believes that better bleaching may be obtained by using chlorine dioxide because less chemical is used and the reaction time is shorter.

A SUMMARY OF THE PROCEDURES USED FOR BLEACHING COLD SODA PULP

TABLE I

Process % Chem.	Other Chem.	%Consist.	Temperature	Reaction Time	% Yield	Wood	Initial Bright.	Final Bright.	Bright. Increment	Reported By
0.96% H_2O_2	0.81% NaOH	13	165° F	-	-	aspen	48.8	66.9	18.1	Foderaro, et. al.
2% H_2O_2	-	-	-	-	-	aspen	70	50	20	McEwen
2% H_2O_2	0.05% $MgSO_4$ 5 % $NaSiO_4$ 1.3 % NaOH	-	185° F	1.75 hr.	-	black birch	-	-	17	Coe and Crosby
1. Acidify with H_2SO_4 to pH 2.5 2. H_2O_2 3. $Na_2S_2O_4$	- pH 6.0	12 4	170° F 140° F	2 hr. 1 hr.	-	beech birch maple	45	80	35	Fennell, Smedberg, and Stalter
2% $NaBH_4$	pH 10	5	35° C	-	-	-	-	-	10.4	Mayer and Donofrio
2% $NaBH_4$	0.4% NaOH	20	75° C	-	-	white birch	45	74	29	Luner
$NaBH_4$	-	15	75° C	3.75 hr.	-	white birch	Hunter Brightnesses -	62.9	16.3	Luner and Supka
1% $Na_2S_2O_4$	0.5% SO_2 Na_3PO_4	-	66° C	0.75 hr.	-	Black birch	-	-	7	Coe and Crosby
10% NaClO	1.3% NaOH	-	32° C	1.25 hr.	-	black birch	-	-	30	Coe and Crosby
11% $Ca(ClO)_2$	3% NaOH 4% $NaSiO_4$	-	-	-	95.7	-	49.3	73.9	24.6	Brown and Monsson

LITERATURE CITED

1. Marton, Renata, Tappi 43, no. 10:826-31 (October 1960)

2. Gierts, H. W., Tappi 44, no. 1:1 - 4 (January 1961)

3. Reichert, J. S., Paper Trade Journal, 135, No. 20:230-243 (Nov. 14, 1952)

4. Foderaro, F. A.; Kenney, F. B.; Raaka, C.; Scott, L. W.; Solari, R. J., "Peroxide Bleaching of Aspen Cold Soda Pulp" Shell Chemical Corp., Union Technical Service Lat. Union, N. J., Jan. 30, 1957.

5. McEwen, Robert L., Paper Trade Journal, 135, No. 20:244-252 (Nov. 14, 1952)

6. Coe, Noel N., and Crosby, Lance H., Tappi 43, no. 1:65-69 (January 1960)

7. Jahne, J. F., and Price, C. E., Tappi 43, no. 7:226-8A (July 1960)

8. Fennell, F. L., Smedberg, G. E., and Stalter, N. J., Tappi 43, no. 11:903-9 (Nov. 1960)

9. Jullander, Ingvar, and Brune, Kurt, Svensk Papperstidn 62, no. 20:728-36 (Oct. 31, 1959)

10. Varsheney, M. C. and Luner, Philip, Tappi 44, no. 4:285-289, (April 1961)

11. Luner, Philip, Tappi 43, no. 10:819-25, (October 1960)

12. Luner, Philip and Supka, Robert, Tappi 44, no. 9:620-624 (Sept. 1961)

13. Mayer, W. C., and Donofrio, C. P., Pulp and Paper Mag. Can. 59 no. 10:157-63, 166 (Oct. 1958)

14. Brown, Kenneth J. and Monsson, William H., Tappi 39, no. 8:592-99 (Aug. 1956)

15. Marpillero, P., "Use of Activated Chlorine for Delignification and Pulp Bleaching", Assoc. Tech. Ind. Papetiere, Bull. no. 2:57-67 (1959); C. A. 53:20792

16. Rapson, Anderson, and Millen, Tappi 42, no. 8:642-49 (Aug. 1959)

Two Stage Peroxide - Borohydride Bleaching of Cold Soda Pulp

EXPERIMENTAL WORK

Objective

The objective of this research project was to investigate the effects of a two stage peroxide-borohydride bleaching procedure on aspen cold soda pulp and to study the relationships between pulping reaction time and bleaching.

Experimental Variables

In order to investigate the values of a two stage peroxide-borohydride bleaching procedure it was first necessary to determine what could be achieved with a single stage. Thus, it was decided to use single stage hydrogen peroxide and sodium hypochlorite stages as initial reactions. The effect of preacidification before the peroxide stage was also investigated. The variables concerned with these experiments may be seen in Table II.

The bulk of the bleaching experiments were two stage peroxide-borohydride. In these experiments the quantity of peroxide and the time of the peroxide stage were varied for each "cook". The variables for these experiments may be seen in Table III.

TABLE II

Experimental Variables
for Single Stage Bleaching Procedures

Identification	Time of "Cook"	Pretreatment with Acid	Percent Chemical	Reaction Time (Hr.)
5-1	0.5	-	5% H_2O_2	3
1-1	1.0	-	5% H_2O_2	3
2-1	2.0	-	5% H_2O_2	3
5-2	0.5	-	10% NaClO	2
1-2	1.0	-	10% NaClO	2
2-2	2.0	-	10% NaClO	2
5-14	0.5	yes	5% H_2O_2	3
1-14	1.0	yes	5% H_2O_2	3
2-14	2.0	yes	5% H_2O_2	3
5-15	0.5	-	5% H_2O_2	2
1-15	1.0	-	5% H_2O_2	2
2-15	2.0	-	5% H_2O_2	2

Note: "Cook" refers to pulping reaction time in hours.

TABLE III

Experimental Variables
for Two Stage Peroxide-Borohydride Bleaching Procedures

Identification	Time of "Cook"	Percent H_2O_2	Reaction Time (Hr.)
5-4	0.5	1	1
1-4	1.0	1	1
2-4	2.0	1	1
5-5	0.5	3	1
1-5	1.0	3	1
2-5	2.0	3	1
5-6	0.5	5	1
1-6	1.0	5	1
2-6	2.0	5	1
5-7	0.5	1	2
1-7	1.0	1	2
2-7	2.0	1	2
5-8	0.5	3	2
1-8	1.0	3	2
2-8	2.0	3	2
5-9	0.5	5	2
1-9	1.0	5	2
2-9	2.0	5	2
5-10	0.5	1	3
1-10	1.0	1	3
2-10	2.0	1	3
5-11	0.5	3	3
1-11	1.0	3	3
2-11	2.0	3	3
5-12	0.5	5	3
1-12	1.0	5	3
2-12	2.0	5	3

Note * "Cook" refers to pulping reaction time in hours.
* All stages were followed by a borohydride stage in which 2% sodium borohydride was applied for 2 hours.

EXPERIMENTAL PROCEDURES

"Cooking" of Pulp

The pulp used in this project was prepared from quaking aspen chips which had been prepared in a commercial chipper in the following manner. Gallon jars were filled with a known weight of chips and then covered with a 4.98% by weight solution of sodium hydroxide. The jars were then rotated at room temperature and atmospheric pressure for periods of 0.5, 1.0, and 2.0 hours.

Refining of Pulp

The treated chips were passed through the breaker plates of a Bauer laboratory refiner twice. Then the fine plates were inserted and the distance between the plates was adjusted so that the motor required three amperes with a normal amount of water running through the refiner. The pulp was passed through the fine plates 5 times.

Screening of Pulp

After refining, the pulp was passed through a Valley Flat bed screen equipped with a 10 cut slotted screen and then through a 50 mesh wire tub screen. The pulp collecting on the 50 mesh screen was taken as the accepts. The dewatered pulp was kept under refrigeration until used.

Hydrogen Peroxide Bleaching

All peroxide bleaching procedures were carried out in polyethylene bags containing 10 g of O.D. unbleached pulp at 15%

consistency. The chemicals used were added according to the following schedule based onthe O.D. weight of Pulp:

1. distilled water to 15% consistency
2. 0.05% magnesium sulfate
3. 5% sodium silicate
4. 1.3% sodium hydroxide
5. 1, 3, or 5% hydrogen peroxide.

Chemicals and pulp were mixed by intermittent kneading. The temperature during bleaching was maintained at 85° C by immersing the bags in a thermostatically controlled water bath. Bleaching times ranged from 1 to 3 hours.

Sodium Borohydride Bleaching

All borohydride bleaching procedures were carried out in polyethylene bags containing 10 g of O.D. unbleached pulp at 15% consistency. The chemicals were added according to the following schedule based on the O.D. weight of pulp:

1. distilled water to 15% consistency
2. 0.5% sodium hydroxide
3. 2.0% sodium borohydride

The temperature was maintained at 75° C during the 2 hour bleaching period.

Sodium Hypochlorite Bleaching

Bleaching ith sodium hypochlorite was also carried out in polyethylene bags containing 10g of O.D. unbleached pulp. Chemicals

were added according to the following schedule based on the O.D. weight of pulp:

1. distilled water to 15% consistency
2. 4% sodium silicate
3. 3% sodium hydroxide
4. 10% available chlorine as sodium hypochlorite

The temperature was maintained at 35° C for 2 hours.

Pre-acidification of Pulp

Ten grams of O.D. unbleached pulp were diluted to 200 ml in a glass beaker. Sulfuric acid (1N) was then added until a pH of 2.5 was obtained. The pulp was allowed to stand for 15 minutes and was then washed on a Buechner funnel.

Washing of Pulp

The pulp was washed after each bleaching stage with distilled water on a Buechner funnel. Approximately 1 liter of water was rinsed through in each of 3 successive washings. (total wash water = 3 liters)

Forming of Handsheets

After washing, the bleached pulp samples were diluted to 2 liters with distilled water. From this, 2 brightness sheets were formed on a Buechner funnel, pressed, and dried according to Tappi Standard T 218 m-48.

Brightness Determination

Brightness values were determined according to Tappi Standard T 217 m-48. The IPC brightness tester was used.

Yield Determination

The conditioned brightness pads backed with standard Wattman No. 2 filter paper were weighed on an analytical balance. Weight determinations were also made on filter paper and the difference was taken as the A.D. weight of the pulp. A moisture determination was run on the scraps of pulp and filter paper in order to ascertain the O.D. weight and the percent yield.

Strength Determination

Zero Span tensile strength was determined according to Tappi Standard T 231 sm-59 using the Schopper tensile tester and attachment. The zero span factor was calculated by dividing the average test value by the total sheet weight of the bleached pulp in grams.

PRESENTATION AND DISCUSSION OF RESULTS

Effects of Single Stage Hydrogen Peroxide Bleaching

The data obtained for brightness, yield, and zero span factor for pulps bleached in a single stage are given in Table IV. Figure 1 graphically represents the difference in brightness obtained by using different bleaching procedures.

Single stage peroxide bleaching of cold soda pulp produces a pulp with good brightness characteristics. The maximum G.E. brightness obtained in this manner was 76.0. Brightness gains for a 3 hour bleaching period are 31.6 points increase for the 0.5 hour pulp, 30.7 for the 1.0 hour, and 29.8 for the 2.0 hour. These large increases account for most of the brightening achieved with the pulp in later stages. Even though the increase in brightness is large, the pulp still possessed a yellowish cast. Pulp which was pretreated with sulfuric acid to a pH of 2.5 was no brighter, than unacidified bleached pulp.

The yields obtained for bleaching sequences 1 and 14 are much lower than would be expected. It is thought that an experimental error was made, and thus, these yields were disregarded. It is assumed that sequences 1 and 14 are similar to sequence 15 and thus, it may be said that a good yield is obtainable with a single stage peroxide bleaching.

Since the yields were disregarded, the actual zero span tests were compared rather than the zero span factor. This comparison shows that strength is relatively unaffected by bleaching except in

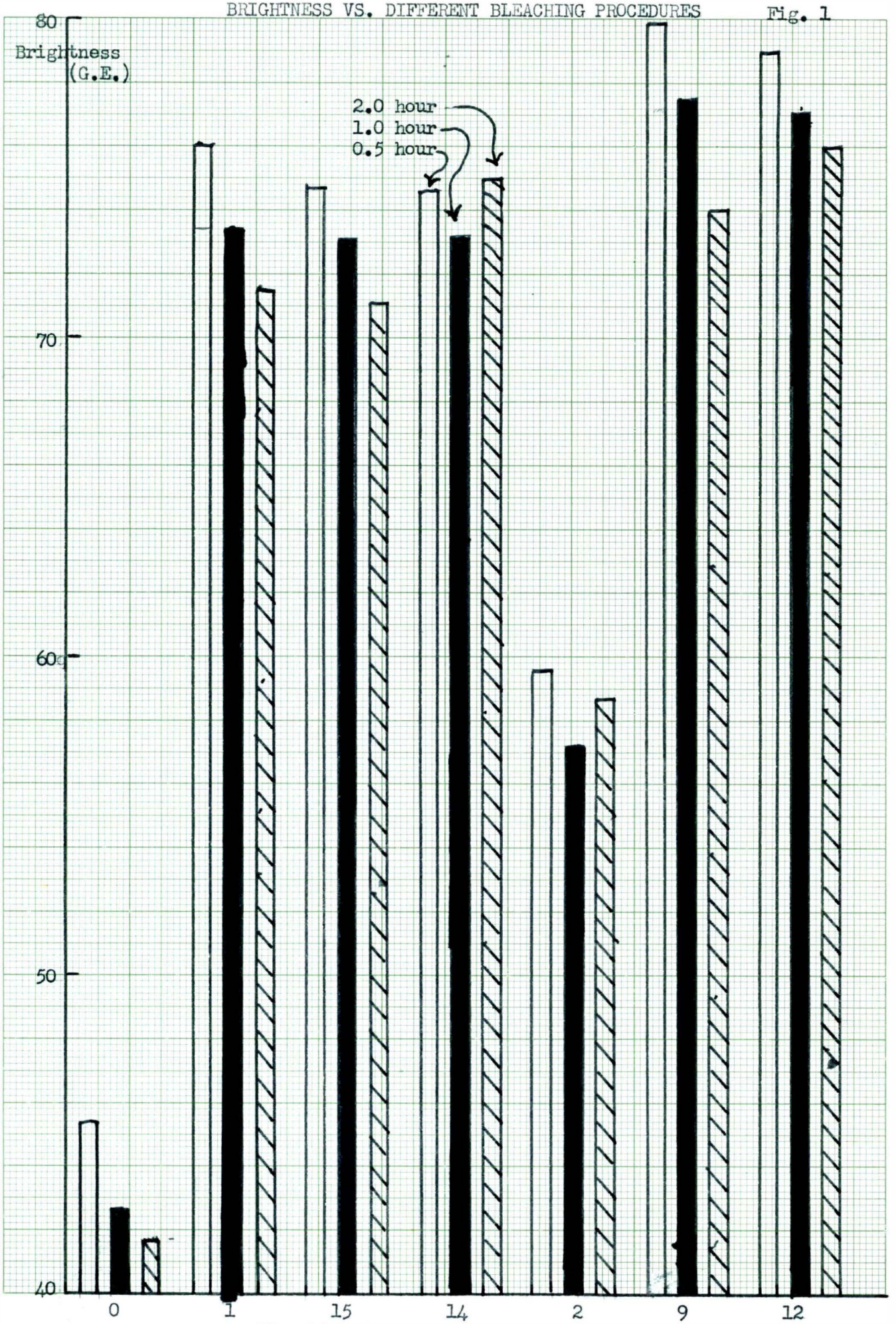
TABLE IV

Experimental Results
of Single Stage Bleaching Procedures

Identification	Brightness (G.E.)	Percent Yield	Zero Span (lbs.)	Zero Span Factor
5-0*	45.4	99.1	48.1	4.85
1-0	42.7	98.5	47.1	4.78
2-0	41.7	96.7	52.3	5.41
5-1	76.0	81.1	46.8	5.75
1-1	73.4	77.5	43.5	5.61
2-1	71.5	81.0	32.5	4.01
5-15	74.7	98.9	47.1	4.99
1-15	73.1	97.4	44.3	4.55
2-15	71.1	95.4	38.1	4.00
5-14	74.6	80.2	47.4	5.91
1-14	73.2	78.2	44.4	5.66
2-14	75.0	80.3	38.8	4.78
5-2	59.6	98.7	56.0	5.67
1-2	57.2	98.8	57.2	5.80
2-2	58.7	89.7	48.9	5.45

*note: The first number represents the time of "cook", the second, the bleaching sequence (see Table II). Thus, 5-0 indicates a 0.5 hour pulp which has not been bleached.

BRIGHTNESS VS. DIFFERENT BLEACHING PROCEDURES Fig. 1



the case of the 2.0 hour pulp where a sharp decrease in strength is noted.

Effects of Single Stage Sodium Hypochlorite Bleaching

Bleaching with alkaline hypochlorite gave brightness gains of 14.2, 14.5, and 17.0 for the 0.6, 1.0, and 2.0 hour pulps, respectively. These gains do not compare with those achieved by a peroxide treatment. The yields and the strength obtained with hypochlorite, however, are higher.

Two Stage Hydrogen Peroxide-Sodium Borohydride Bleaching

The data obtained for brightness, yield, and zero span factor for pulps bleached with 2 stages (peroxide-borohydride) are given in Table V. The addition of a sodium borohydride stage after the peroxide treatment provides approximately 5 to 6 points increase in brightness. Although yellowness was not determined, peroxide bleached pulp treated with sodium borohydride does not appear as yellow as that treated with a hydrosulfite. Despite the fact that sodium borohydride is expensive and did not provide a large increase in brightness, it is thought that after more research its use as a bleaching agent may be very beneficial. Accompanying the increase in brightness caused by a borohydride treatments is a significant decrease in yield and an increase in strength.

Effects of Peroxide Bleaching Time on Brightness

The effects of peroxide bleaching time in a 2 stage peroxide-borohydride bleaching treatment on brightness are represented in

TABLE V

Experimental Results
of Two Stage Peroxide-Borohydride Bleaching Procedures

Identification	Brightness (G.E.)	Percent Yield	Zero Span Factor	Brightness Gain	Zero Span Differential*
5-4**	66.5	93.5	4.37	21.1	-.48
1-4	65.8	95.0	5.85	23.1	1.07
2-4	59.8	96.4	5.82	18.1	0.41
5-5	76.0	92.6	6.05	30.6	1.20
1-5	74.4	95.4	5.73	31.7	0.95
2-5	66.9	91.0	6.65	25.2	1.24
5-6	77.4	94.3	6.83	32.0	1.98
1-6	79.5	92.1	6.87	36.8	2.09
2-6	74.7	92.1	6.06	33.0	0.65
5-7	67.4	93.8	6.23	22.0	1.38
1-7	66.1	95.6	5.12	23.4	0.34
2-7	62.4	95.9	4.82	20.7	-.59
5-8	75.9	94.6	5.81	30.5	0.96
1-8	73.5	95.2	5.69	30.8	0.91
2-8	66.8	93.0	5.71	25.1	0.30
5-9	79.9	9.36	6/29	34.5	1.44
1-9	77.5	9.30	6.40	34.8	1.62
2-9	74.0	93.2	4.98	32.3	-.43
5-10	63.2	94.6	6.48	16.8	1.63
1-10	62.0	93.2	6.05	19.3	1.27
2-10	69.1	94.0	4.96	27.4	-.45
5-11	76.0	91.1	7.05	30.6	2.20
1-11	73.5	91.7	5.20	30.8	.42
2-11	63.1	95.2	4.98	21.4	-.43
5-12	79.0	92.6	4.98	33.6	0.13
1-12	77.1	96.3	6.15	34.4	1.37
2-12	76.0	95.7	5.72	34.3	0.31

*note: This represents the difference between the bleached and the unbleached pulps.

** The first number represents the time of "cook", the second, the bleaching sequence (see Table III).

Figures 2, 3, and 4. Brightness increases rapidly during the initial period of bleaching, reaching a maximum between 1 and 2 hours. After this there is generally a decrease in brightness. The maximum brightness obtained was 7 9.5 by applying 5% peroxide to the 0.5 hour pulp for 2 hours followed by a borohydride stage. It is thought that perhaps a higher value could be obtained after 1 hour of bleaching under these conditions because this point in Figure 6 seems low when compared with the others. This indicates that a brightness above 80 could be obtained.

Effects of Peroxide Bleaching Time on Strength

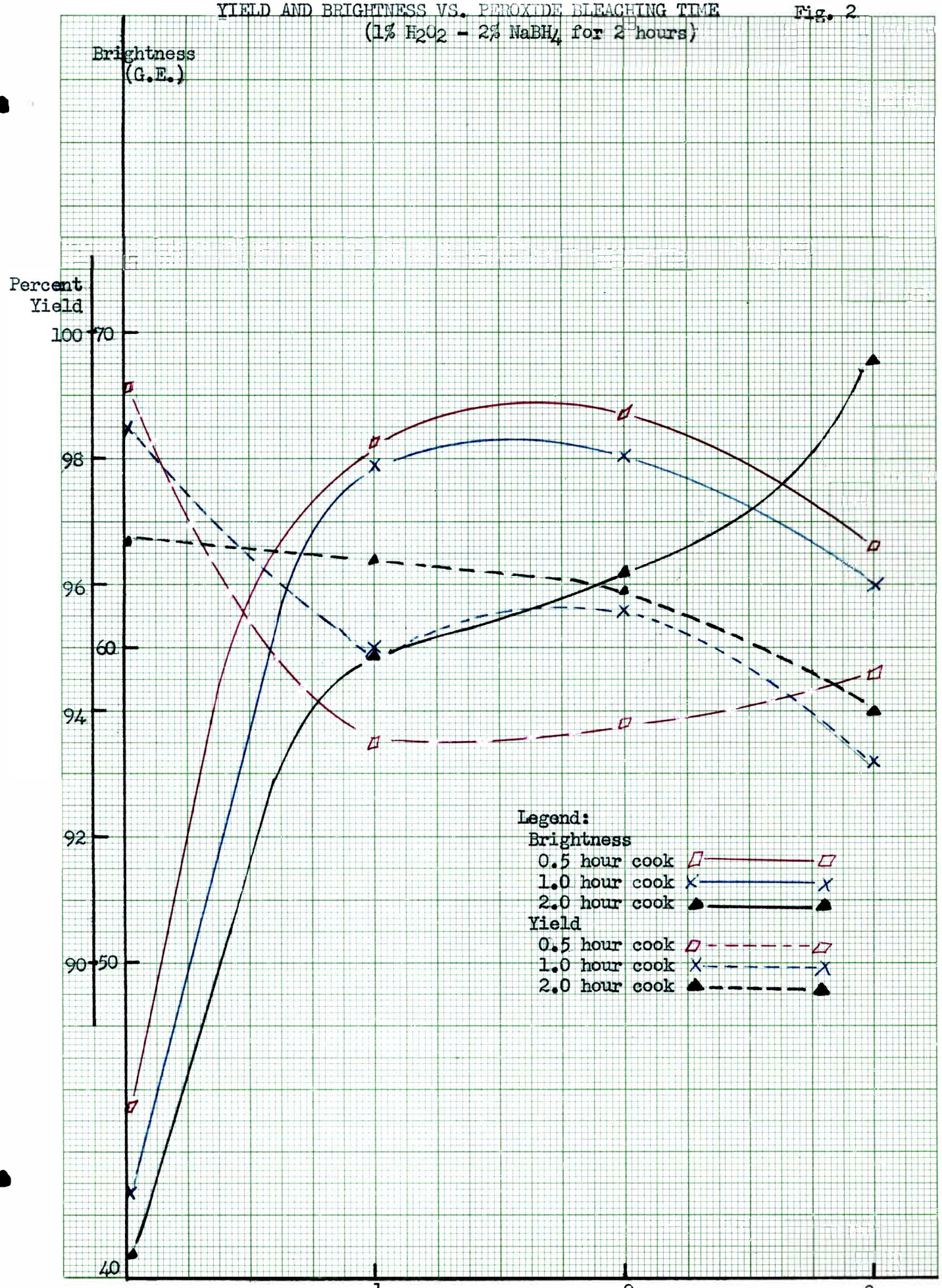
Strength increases sharply and then decreases with increasing bleaching time. This is especially noticable when a higher concentration of peroxide is used. Pulp which was treated with 5% peroxide for 1 hour has the greatest strength, reaching a maximum factor of 6.87. The fact that strength increases and then decreases again with increasing bleaching time would indicate that two bleaching reactions are involved. In the first the pulp is purified and in the second, the strength giving fibers, themselves, are attacked.

Effects of Peroxide Bleaching Time on Yield

The effects of peroxide bleaching time in a 2 stage peroxide-borohydride treatment on yield are also represented in Figures 2, 3, and 4. The yield exhibits a downward trend as bleaching time increases. In all cases, the yield substantially decreases after 1 hour of peroxide treatment. In those pulps where the pulp has

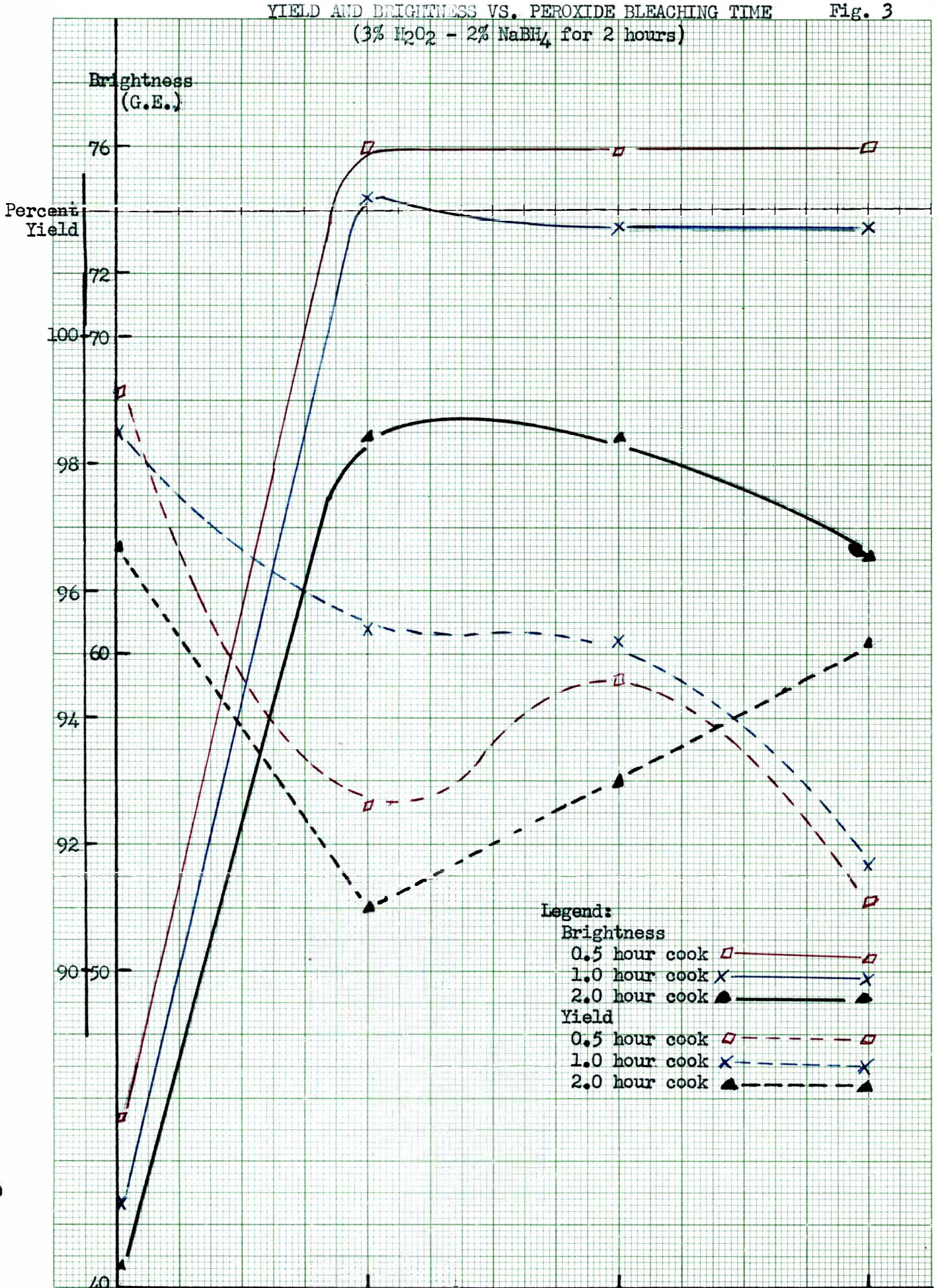
YIELD AND BRIGHTNESS VS. PEROXIDE BLEACHING TIME Fig. 2

(1% H_2O_2 - 2% $NaBH_4$ for 2 hours)

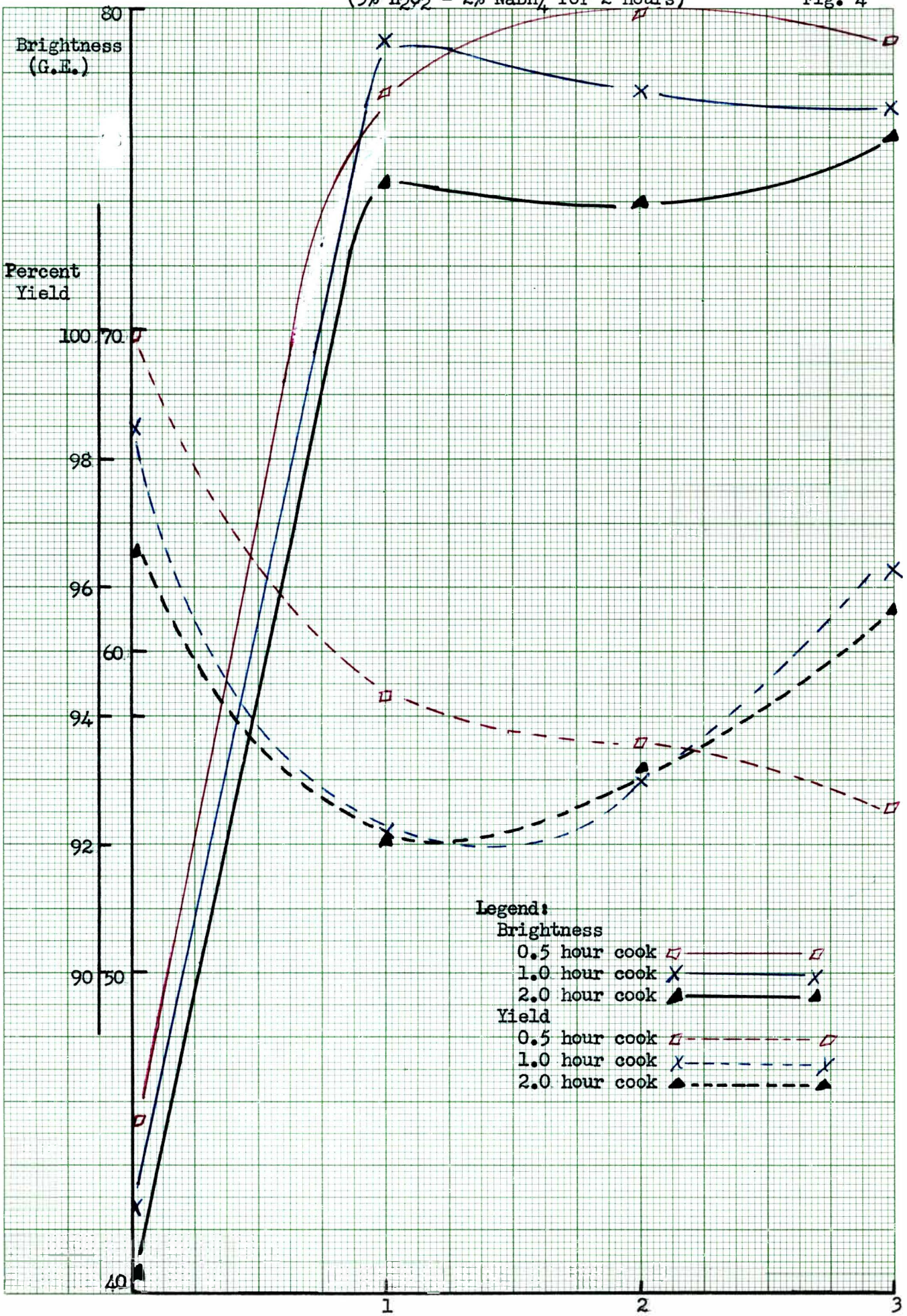


YIELD AND BRIGHTNESS VS. PEROXIDE BLEACHING TIME Fig. 3

(3% H_2O_2 - 2% $NaBH_4$ for 2 hours)



YIELD AND BRIGHTNESS VS. PEROXIDE BLEACHING TIME
(5% H_2O_2 - 2% $NaBH_4$ for 2 hours) Fig. 4



been subjected to more extreme conditions (3% H_2O_2, 2.0 hour pulp, 5% H_2O_2, 1.0 hour and 2.0 hour pulp) both in pulping and in bleaching, the yield tends to increase after the initial decrease. This final increase in yield may be the result of the formation of insoluble peroxide residues.

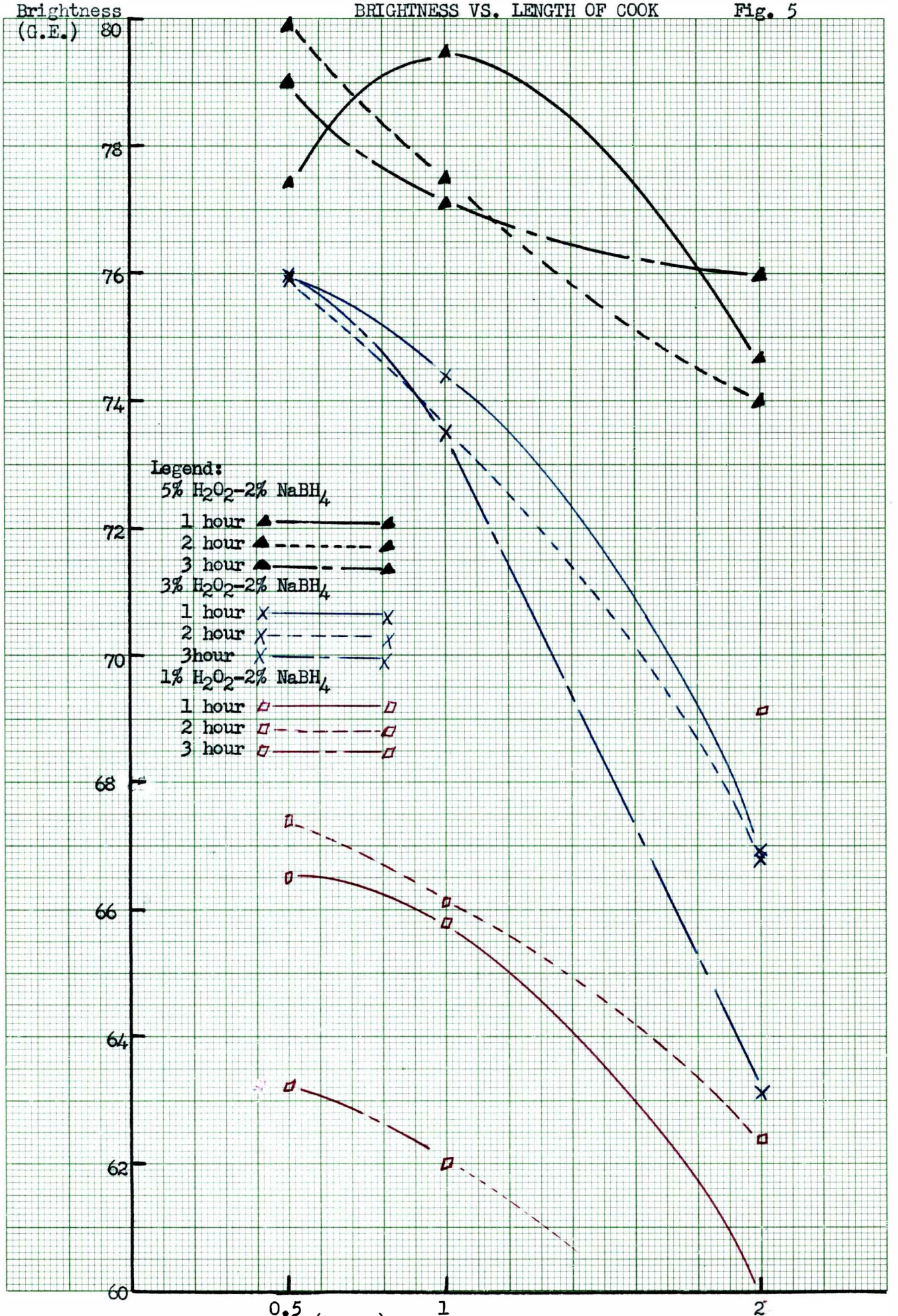
Effects of Pulping Reaction Time on Brightness

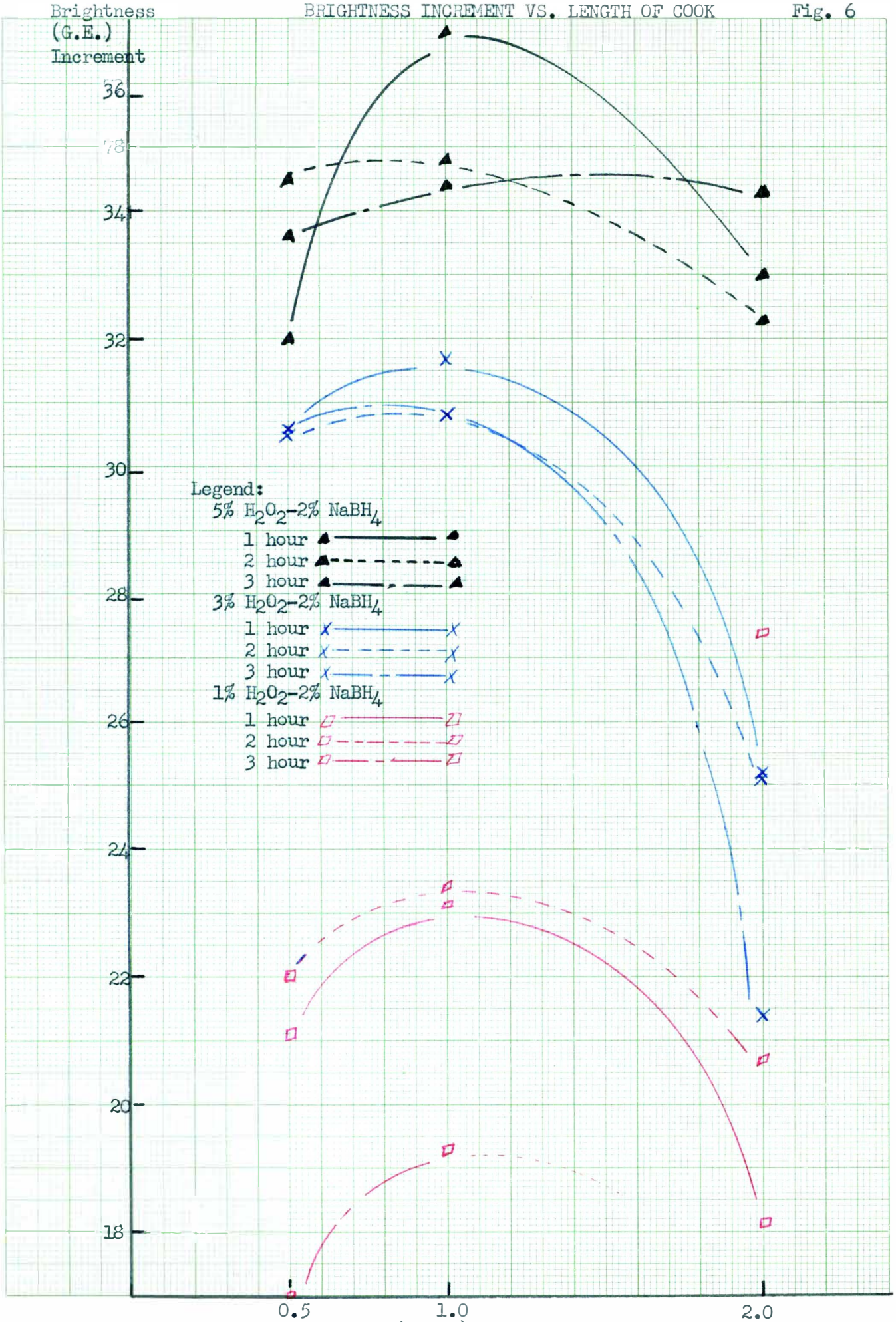
The effects of pulping reaction time on brightness are shown graphically in Figure 5. Figure 6 shows the effects of pulping reaction time on the brightness increment.

Generally, higher brightnesses may be obtained from those pulps which were not subjected to an extensive pulping reaction. This is true of both bleached and unbleached pulps. This phenomena results from the formation of dark coloring materials by caustic soda and wood. The amount of coloring material formed increases with reaction time.

Although brightness decreases with length of cook, the ease of bleaching is affected very little after moderate pulping reactions. A slight increase in the brightness increment is noted between the 0.5 hour and the 1.0 hour pulps. This is followed by a sharp decrease after 2.0 hours of pulping. This indicates that not only does the pulp become darker, but also harder to bleach after long pulping periods. This fact indicates that perhaps bleaching during the pulping reaction is a good idea. If the coloring materials are bleached as they form, perhaps higher brightnesses could be obtained.

BRIGHTNESS VS. LENGTH OF COOK Fig. 5




Brightness (G.E.) Increment
BRIGHTNESS INCREMENT VS. LENGTH OF COOK
Fig. 6
36
34
32
30
28
26
24
22
20
18
Legend:
5% H2O2-2% NaBH4
1 hour
2 hour
3 hour
3% H2O2-2% NaBH4
1 hour
2 hour
3 hour
1% H2O2-2% NaBH4
1 hour
2 hour
3 hour
0.5
1.0
2.0
Length of Cook (hours)

Effects of Pulping Reaction Time on Strength

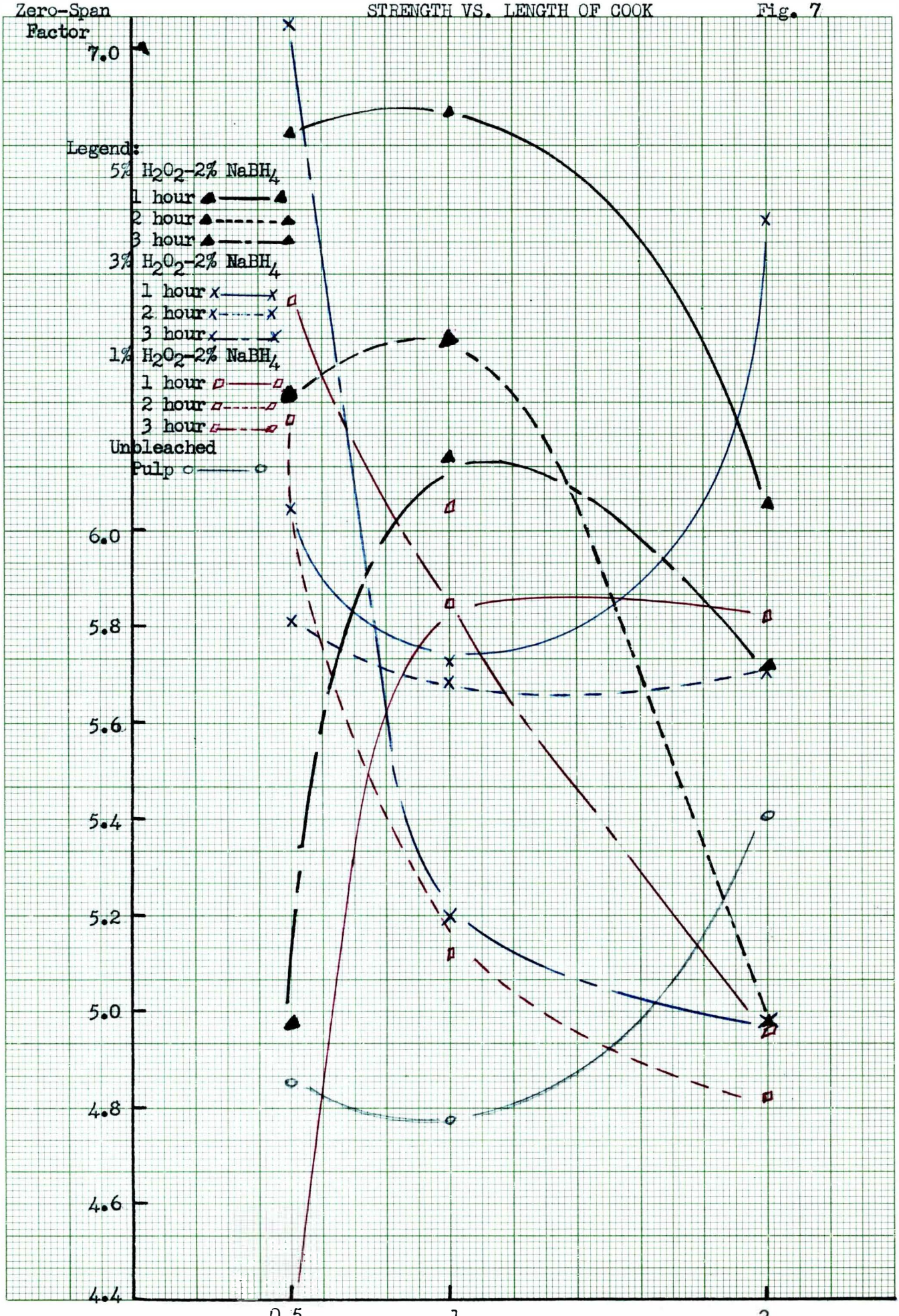
The efects of pulping reaction time on strength are represented graphically in Figure 7, on the strength increment in Figure 8.

The zero span factor of the unbleached pulp decreases with increasing cooking time and then increases more sharply. A maximum brightness of 79.9 was attained with the 1.0 hour pulp to which 5% peroxide and then borohydride was applied. This pulp also possessed one of the highest strengths.

It is interesting to note that the difference in strength falls off in much the same manner as the difference in brightness, especially when 5% peroxide is used. The similarity of these curves indicates that those pulps which are bleached to a higher brightness are also purified to a greater extent and that brightness and strength are related. However, all attempts to graph brightness versus strength resulted in a chaotic confusion of points.

If the strength is increased by bleaching, then it is very probable that these methods of bleaching may be considered as a continuance of the cooking cycle in that the gamma and beta celluloses are removed. This would also mean that the coloring material may be somehow connected with the cellulose. It would be interesting to analyze these bleached pulps to determine what is happening to the structure of the pulp chemically.

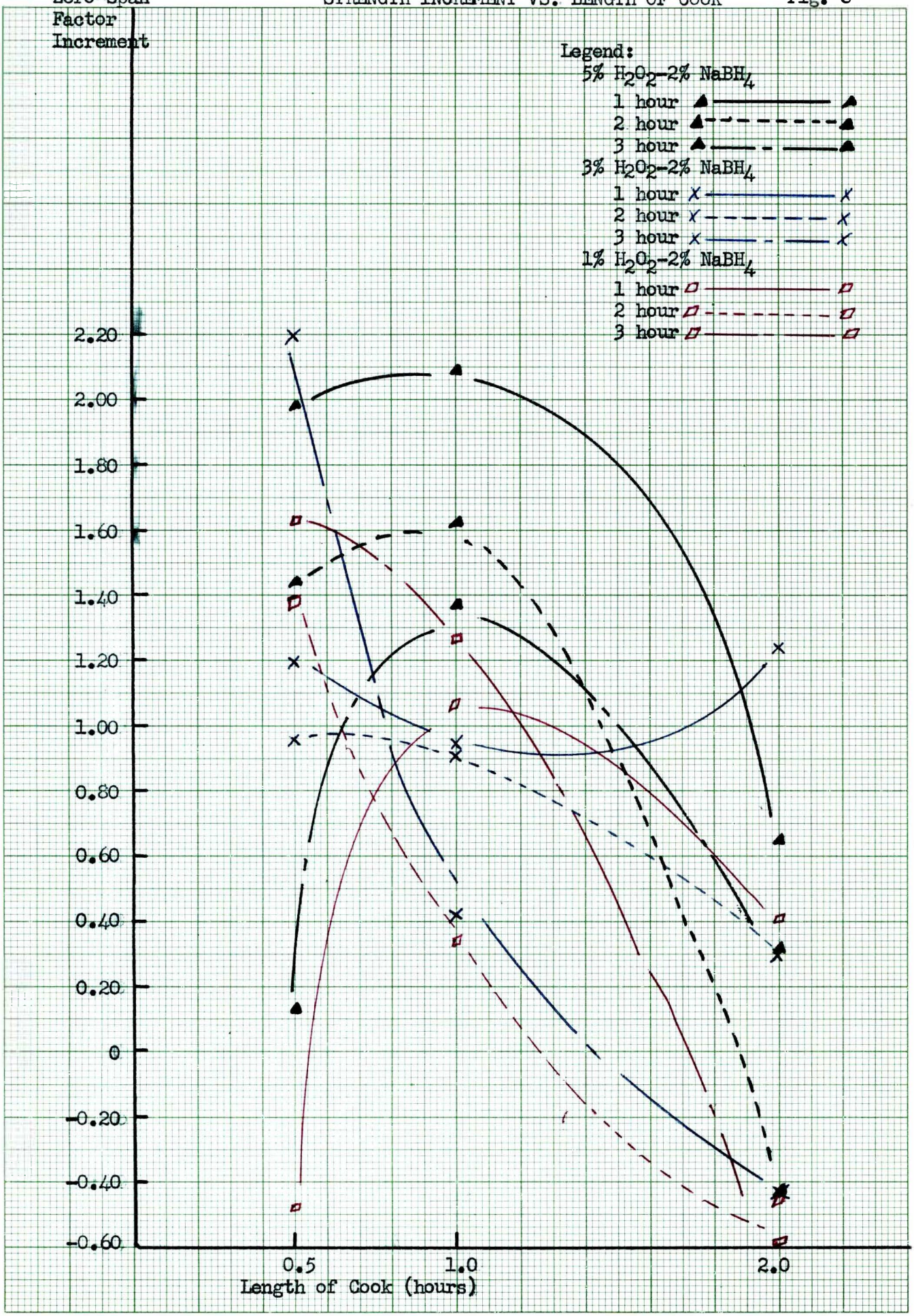
Noting these similarities between strength and brightness, it may be concluded that bleaching affects the 0.5 hour pulp moderately both with an increase of strength and of brightness. Bleaching affects the 1.0 hour pulp most and has little effect upon the 2.0


Zero-Span Factor
STRENGTH VS. LENGTH OF COOK
Fig. 7
7.0
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
Legend:
5% H_2O_2-2% $NaBH_4$
1 hour
2 hour
3 hour
3% H_2O_2-2% $NaBH_4$
1 hour
2 hour
3 hour
1% H_2O_2-2% $NaBH_4$
1 hour
2 hour
3 hour
Unbleached Pulp
0.5
1
2
Length of Cook (hours)

Zero-Span Factor Increment

STRENGTH INCREMENT VS. LENGTH OF COOK

Fig. 8



hour pulp. This indicates a maximum cooking time of 1.0 hour if the optimum brightness and strength are to be obtained.

Effects of Pulping Reaction Time on Yield

The yields obtained using a two stage peroxide-borohydride bleaching procedure ranged between 91 and 96.5% based on the O.D. unbleached pulp. The data for yield versus length of cook is plotted in Figure 9. No conclusions can be drawn as to the relationship between pulping reaction time and yield.

Effects of Percent Peroxide on Brightness

The highest brightness increment is achieved by using 5% peroxide in the first stage. Perhaps higher brightnesses may be obtained if an even greater percentage were used, but the costs of this method would have to be investigated before the commercial value of such strong bleaching would be considered.

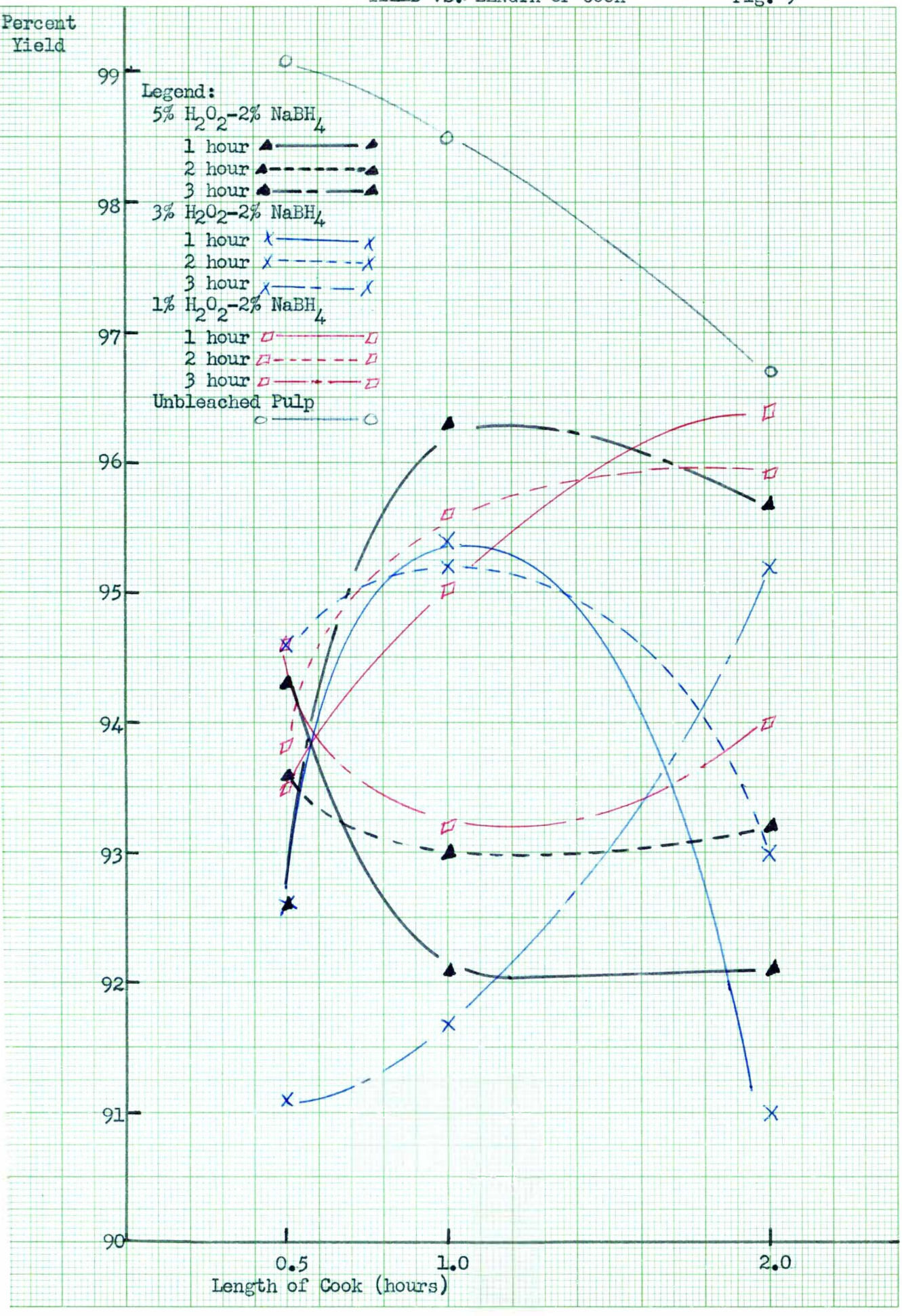
Effects of Percent Peroxide on Strength

Use of 5% peroxide for a 1 hour period produces the maximum strength pulp. No conclusion can be reached concerning the variance in strength and the use of 3 or 1% peroxide. These results may be obscured by the addition of the second stage of borohydride.

Effects of Percent Peroxide on Yield

No conclusions can be drawn concerning the effect of the percent peroxide on yield. This relationship may also be obscured by the second stage borohydride treatment.

YIELD VS. LENGTH OF COOK Fig. 9



CONCLUSIONS

1. Aspen cold soda pulp can be bleached to a brightness of 76.0 using a single stage hydrogen peroxide treatment.
2. A maximum brightness of 79.9 was achieved by applying 5% hydrogen peroxide for 2 hours at 85° C and then 2% sodium borohydride for 2 hours at 75° C to a 0.5 hour pulp.
3. The optimum length of time for peroxide bleaching is between 1 and 2 hours.
4. The optimum length of pulping is between 0.5 and 1 hour.
5. The optimum quantity of peroxide to use is 5 percent.
6. At present it is difficult to recommend sodium borohydride as an effective commercial bleaching agent due to its high cost. However, it is thought that as it is a relatively new chemical, its cost will decrease. Excellent beginnings have pointed to its potential as an effective bleaching agent, but much more research remains to be done concerning its use. Nevertheless, it is thought that sodium borohydride will find a place as an excellent bleaching agent.