



Western Michigan University
ScholarWorks at WMU

Paper Engineering Senior Theses

Chemical and Paper Engineering

12-1975

Two-Stage Peroxide-Hydrosulphite Bleaching of Groundwood Pulp

Richard Daniel Hyatt
Western Michigan University

Follow this and additional works at: <https://scholarworks.wmich.edu/engineer-senior-theses>



Part of the Wood Science and Pulp, Paper Technology Commons

Recommended Citation

Hyatt, Richard Daniel, "Two-Stage Peroxide-Hydrosulphite Bleaching of Groundwood Pulp" (1975). *Paper Engineering Senior Theses*. 235.

<https://scholarworks.wmich.edu/engineer-senior-theses/235>

This Dissertation/Thesis is brought to you for free and open access by the Chemical and Paper Engineering at ScholarWorks at WMU. It has been accepted for inclusion in Paper Engineering Senior Theses by an authorized administrator of ScholarWorks at WMU. For more information, please contact wmu-scholarworks@wmich.edu.



TWO-STAGE PEROXIDE-HYDROSULPHITE
BLEACHING OF GROUNDWOOD PULP

by
Richard D. Hyatt

A Thesis Submitted To The Faculty
of the Department of Paper Science & Engineering
in partial fulfillment
of the
Degree of Bachelor of Science

Western Michigan University
Kalamazoo, Michigan

ABSTRACT

The conditions and chemicals for the use of hydrogen peroxide, sodium hydrosulphite and zinc hydrosulphite for the bleaching of groundwood pulp are discussed. Previous research provided guidelines for establishing optimum conditions for temperature, time, pH, consistency and type of buffer. The research carried out determined optimum conditions for a two-stage peroxide-hydrosulphite sequence. The use of an HCl extraction prior to bleaching was found to be as effective as EDTA for the removal of heavy metals. The combination of peroxide-hydrosulphite gave a brightness rise of 26 G. E. points while hydrogen peroxide alone gave 22.2 points and hydrosulphite alone gave 8.7 to 11 points. The effects of combination bleaching are not totally additive.

TABLE OF CONTENTS

	PAGE
GENERAL COMMENTS	1
HISTORICAL REVIEW OF PEROXIDE.	2
CHEMISTRY OF PEROXIDE BLEACHING.	4
PEROXIDE BLEACHING TECHNOLOGY.	6
Percent Peroxide.	6
Alkalinity.	7
Pulp Consistency.	8
Temperature	9
Time	9
Reducing and Neutralizing Treatment	9
Variables in Pulp and Water	9
Chemicals Used in Peroxide Bleach System.	10
Hydrogen Peroxide.	10
Sodium Peroxide	11
Sodium Silicate	11
Caustic Soda	12
Magnesium Sulfate.	12
Sequestering Agents.	12
Neutralizing and Reducing Agent.	13
HISTORICAL REVIEW OF HYDROSULPHITES.	14
CHEMISTRY OF HYDROSULPHITE BLEACHING	15

TABLE OF CONTENTS (Cont.)

HYDROSULPHITE BLEACHING TECHNOLOGY	17
Type of Hydrosulfite.	17
Chemical Concentration.	17
Pulp Consistency	18
Temperature	18
Retention Time.	19
pH.	19
Oxygen.	21
Sequestering Agents	22
Washing	22
Brightness Reversion.	23
TWO STAGE PEROXIDE HYDROSULPHITE BLEACHING	24
OBJECTIVE	25
EXPERIMENTAL SECTION.	26
EQUIPMENT AND PULP CONSIDERATIONS	26
EXPERIMENTAL CONDITIONS	27
OBSERVATIONS.	29
DISCUSSION OF GRAPHS.	30
SUGGESTIONS FOR FURTHER STUDY	32
CONCLUSION	33
BIBLIOGRAPHY.	34

ACKNOWLEDGEMENTS

This author would like to extend his thanks to Dr. Stephen I. Kukolich for his patients, and willingness to assist me whenever the need arose. Also my thanks to Diamond Shamrock Corporation and Virginia Chemicals Inc. for the chemicals and advice supplied me at the outset of my thesis.

GENERAL COMMENTS

According to Andrews (3) color of wood depends upon its non-carbohydrate content. Lignin (being a carbohydrate polymer) is believed to be white in its native state. The color of wood is largely attributed to extraneous compounds. However, lignin contains sites that can be readily converted to chromophonic groups. Because of high temperature and new surfaces continually being exposed to air oxidation, mechanical pulping provides the opportunity for development of color.

Because lignin is a large percentage of groundwood it is necessary to remove the color components without rendering the lignin soluble. Peroxides and/or hydrosulphites are used to decolor groundwood without lowering yield significantly.

HISTORICAL REVIEW OF PEROXIDE

In 1940 the peroxide process for bleaching mechanical pulp was first put into commercial operation. By 1950 the process was in operation in 24 mills with a daily bleaching capacity of 1250 tons (1).

There is not much literature on peroxide prior to 1930. The earliest reference was a German patent issued in 1905, the process was multistage and included bleaching with peroxide and chlorine. Not much was done for another 20 years when a U.S. patent was issued describing a process of treating mechanical pulp with peroxide to achieve better separation of fibers and formation of a stronger, tougher, cleaner, more uniform paper.

After this point a lot of research was carried out and from about 1934 on many papers were written and patents issued dealing with various aspects of peroxide bleaching.

Of the work carried out the most important seems to have been that done at the Institute of Paper Chemistry in 1937. The project was sponsored by the DuPont Company and the data obtained led to the conclusion that peroxide bleaching would increase the brightness of wood pulps to a considerable degree with little or no degradation of the cellulosic or non-cellulosic constituents of the wood fiber, i.e., the strength of wood pulps is not impaired by peroxide bleaching, and there is little or no weight loss in the bleaching operation (1).

At this time many newsprint producers were faced with the prospect of converting their mills to produce a higher grade of paper. Mechanical pulps imparted desirable characteristics but the brightness was too low for extensive use in production of higher quality papers. There existed no technology for raising the brightness to the desired level. A study by DuPont in their lab established the best conditions for peroxide bleaching of groundwood and in 1941 at the Norfolk mill of the St. Regis Paper Company the first extensive mill trial took place. The bleaching operation was successful and resulting in a furnish of 60% bleached groundwood. This established new standards of quality for the industry while at the same time reducing costs.

CHEMISTRY OF PEROXIDE BLEACHING

Peroxide is an oxidative chemical used to bleach pulp. It was found that the bleaching rate increases with pH as $\text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{HOO}^-$, the addition of alkali causes hydrogen ions to be used up thus forcing the reaction to the right increasing the concentration of perhydroxyl ions (HO_2^-). It is generally acknowledged that the perhydroxyl ion is the active bleaching species (1, 2, 4, 6).

An optimum pH of 10.5 is required to obtain greatest bleaching efficiency. If pH is much higher than 10.5 the alkali will cause a "browning" of pulp and more peroxide would have to be used to obtain a specific brightness. (Browning is a reaction caused by the pulp absorbing alkali components which in turn darken the pulp.)

Temperature effects the dissociation of peroxide, increased temperature implies increased dissociation. It would seem as though raising the temperature would allow greater bleaching efficiency but this is only true to a point. If the temperature is raised to high it increases the reactivity of alkali with pulp thereby increasing the "browning" reaction. Both temperature and pH must be balanced to suppress the "browning" reaction and allow maximum brightness to be obtained.

Peroxide decomposition is catalyzed by such heavy metal ions as copper, managanese, nickel and also some types of enzymes (5, 6). The

decomposition takes place in the form of $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$. This is a competing reaction and takes place all of the time, however, heavy metal ions speed it up. As it does nothing to aid in bleaching it is a waste of peroxide and is to be avoided.

PEROXIDE BLEACHING TECHNOLOGY

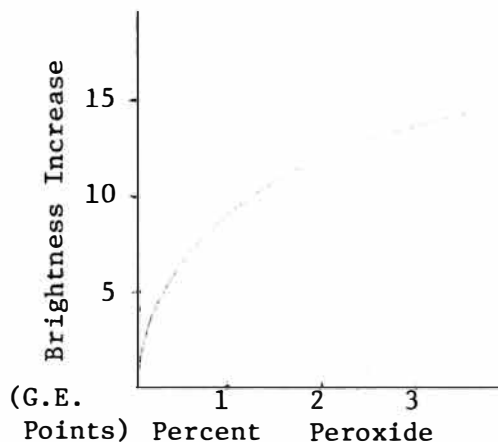
Peroxide bleaching has little effect on bulk, freeness, or strength characteristics of groundwood pulps and it aids in producing a cleaner and more absorbent pulp with improved formation and printing properties.

The major advantages of using peroxides with groundwood are substantial brightness gains of 10 or more G.E. points with excellent brightness stability and low yield losses.

Basic to the considerations of bleaching is the wood to be bleached. Final brightness is effected by initial wood brightness, species of wood (i.e., Hemlock and certain pine give very poor brightness), and the age of the wood, greenwood is more easily bleached than wood that has been in storage for six months (1, 2, 6).

Percent Peroxide

Percent peroxide used in bleaching is set by desired brightness, initial brightness, pulp type and quality, as well as bleaching density (increased density implies decreased amount of peroxide and temperature). In industrial situations the amount is between 1 and 2%, based on bone dry weight of pulp, depending upon the above named factors. However, there is a general rise in brightness with increasing concentrations of peroxide, the curve looking something like this:



The gain in brightness rises sharply for the first few percent then levels off. It would seem possible to bleach to brightnesses in excess of 80% if one would set conditions properly and just add a high percentage of peroxide. Indeed I will try this.

Alkalinity

All sources reviewed seemed to have a different range for pH depending upon, primarily, temperature and consistency but they all seemed to be in general agreement on the following:

1. A pH of between 10 and 11 is optimum.
2. For low consistencies (less than 6%), a higher pH is best.
3. For high consistencies (above 12%) a lower pH is acceptable (3).
4. NaOH is a good pH adjuster initially but,
 - A. The reaction of active alkali with pulp causes active alkali to be rapidly consumed, causing a sharp pH decrease and cessation of perhydroxyl formation.
 - B. Chemicals similar to NaOH are preferentially absorbed into the pulp "browning" reaction, increasing the burden on peroxide (4).

Buffered or bound alkali sources do not have the above disadvantages

because they release alkalinity slowly through the bleaching period. Sodium silicate, 41°Bé is almost always chosen because it is a low cost alkali buffer, it acts as a peroxide bleach stabilizer, a metal surface passivator and a wetting agent (3, 4, 6).

Total alkali of between 0.75 and 1.50% is the accepted range. At consistencies below 12%, 1.5% total alkali gives highest brightness, above 20% consistency the difference between 0.75 and 1.50% total alkali is almost non-existent.

Stove (4) found that where 40% or more of the total alkali was silicate the brightness was the same as using 100% silicate.

Again pH only allows conditions to exist for H_2O_2 to dissociate into perhydroxyl ions.

Pulp Consistency

With all variables constant it would seem logical that if consistency were increased it would allow peroxide to react more quickly with pulp. Indeed, this is the case. With all other variables held constant increasing consistency causes a brightness increase that is fairly linear up to around 25% where it begins to level off (2, 6, 8). After about 35% there seems to be no justification for increasing consistency any further.

Industrially, increased consistency offers the advantages of improved chemical efficiency with a resultant decrease in bleaching costs and a shorter retention time to achieve the same brightness level.

Temperature

An example was given in Tappi Monograph 27, "bleaching mechanical pulp at 12% consistency and 110°F requires 1.2 hours for completion, whereas at 90°F the bleaching will be substantially complete in about 1.8 hours". As temperature increases the time required to achieve a specified brightness decreases. The generally accepted temperature range is between 100 and 120°F. Below 100°F wastes time and much above 120°F furthers the "browning" reaction and causes the peroxide more work.

Time

Time is relative to the above mentioned variables. Generally speaking the longer the retention time the brighter the pulp. The practical limit would seem to be two to three hours.

Reducing and Neutralizing Treatment

This is done after the bleaching cycle is complete. The residual peroxide is destroyed, generally with SO_2 or a derivative of SO_2 . The reducing agent is added in order to lower the pH to a value of 6 or 7. With good mixing the reaction is completed almost instantly.

Variables in Pulp and Water

It seems as though bleaching immediately after grinding yields better brightness results than storing and then bleaching. However,

good bleaching results can be obtained if groundwood is stored properly. Should molding or spoilage of pulp occur there is an adverse effect on bleaching.

Species of wood effects bleaching, in order of decreasing response (6); poplar, birch, spruce, eastern softwood, pines, hemlocks, and Douglas fir. Another pulp variable is the amount of heartwood. The less heartwood the better for increasing brightness (3, 6).

Colored impurities, waste reducing agents, bacteria, and heavy metals in water will all use up peroxide and if present in sufficient quantities a lowering of final brightness will be realized. Colored impurities and heavy metals can be taken care of with a chelating agent like STPP, DTPA or EDTA or magnesium sulfate. Bacteria can be controlled through heat, chlorinating agents, oxidizing agents, and other bactericides.

Chemicals Used In Peroxide Bleach System

Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) marketed principally as aqueous solutions containing 35, 50 and 70% hydrogen peroxide by weight. The following table gives details on each solution at 20°C;

<u>% peroxide</u>	<u>% active oxygen</u>	<u>density</u>	<u>lb/gal</u>
35	16.5	1.1327	9.44
50	23.5	1.1957	9.97
70	32.9	1.2836	10.7

Hydrogen peroxide is usually shipped in 250 lb. aluminum drums and in aluminum tank cars. It must be kept free from metallic impurities which would cause catalytic decomposition.

Sodium Peroxide

Sodium peroxide (Na_2O_2)₄ is a pale yellow solid shipped in 400 lb. drums. It contains 19.6% active oxygen. It is stable when dry and kept in air tight containers. Sodium peroxide cannot be used alone because its alkali content exceeds the amount necessary for best results. Sulfuric acid may be added to the bleach solution to reduce alkalinity.

Sodium Silicate

In bleaching process its color should be water white and as free as possible from heavy metal impurities. Silicate solutions or solid are available. Sodium peroxide and sodium silicate together supply more alkali than is required for bleaching and therefore the silicates principle value is in its SiO_2 content rather than its Na_2O content (2). When sodium silicate is used with hydrogen peroxide required alkalinity is most economically supplied by the addition of sodium hydroxide.

Sodium silicate acts as a detergent and a wetting agent. It also acts as a buffer. It forms a protective coating on metal surfaces and inhibits corrosion. When sodium silicate and a trace of magnesium sulphate are mixed they react to form a stable colloidal suspension of magnesium silicate which aids in inactivating metallic decomposition (3).

In most references 5% of sodium silicate (41.5° Bé containing 29% SiO_2 and 8.9% Na_2O) based on dry pulp was the recommended amount.

Caustic Soda

Caustic soda is the cheapest chemical for raising alkalinity. As it possesses no buffering properties and should be used with sodium silicate.

Magnesium Sulfate

Available as hydrated crystalline Epson salt ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$). It acts to stabilize peroxide solution by inhibiting the catalytic effects of iron, copper, and manganese all of which are common in pulpwood and mill water. Only small amounts are necessary to obtain good results from its use, approximately 0.05% on bone dry pulp (1, 2, 3, 6).

Sequestering Agents

Due to the catalytic nature of heavy metal ions on peroxide it is necessary to remove them for efficient bleaching. The source of heavy metals is not only the water but also the pulp. As noted by Gupta and Mutton (9), groundwood acts as a low capacity ion-exchanger with a great affinity for heavy metals and less affinity for alkaline earth metals. Divalent metals are easier to remove than trivalent metals. Deionization of groundwood is most effectively carried out by using a sequestering agent at a low pH.

A chelating agent forms complexes with heavy metals and renders them harmless insofar as catalytic decomposition of peroxide is concerned. Several were mentioned as being effective, they include; sodium tripolyphosphate (STPP), Bis-phosphonylethylphosphonic acid pentasodium salt (MTPP), diethylenetriamine-pentaacetic acid (DTPA) and ethylene-diaminetetracetic acid (EDTA).

All of the above mentioned chelating agents work but it was stated the DTPA worked well with peroxides and STPP worked well with hydro-sulfites. At any rate anything is better than nothing.

Neutralizing and Reducing Agent

Reducing agents, such as sulfur dioxide and sodium bisulfite are used to neutralize pulp slurries after the bleaching process. In some cases sulfuric acid has been used for lowering the pH to the desired level.

The purpose of a reducing agent is to stop the reaction of peroxide on the pulp. An acid reducing agent has several desirable characteristics. It neutralizes the alkali remaining in the pulp. It reduces to the colorless form traces of highly colored ferric iron normally present in bleached pulp. It also destroys residual peroxide.

The reducing agent is added until the pH is at the desired level, normally 6 to 7.

HISTORICAL REVIEW OF HYDROSULPHITES

Hydrosulphites are not the principal reducing agents commercially used for bleaching pulp, they were discovered in 1789 by Berthollet when he noticed that iron dissolved in sulfurous acid without evolving gas.

The first known application of hydrosulphites to pulp brightening was in 1927 by Hirschkind (2), he also obtained several patents. He found hydrosulphites to be more effective than sodium or calcium bisulfite when brightening pulp.

About the same time (1929) investigations by Andrews led to the use of zinc hydrosulphite to brighten newsprint groundwood on a mill scale, in 1932.

During the 1930's this method was adopted by most West Coast newsprint mills.

Early on it was found that poor mixing and aeration caused brightness to be much lower than laboratory tests. Plus, fourdrinier wire life and drier felt life decreased with increasing use of white water containing zinc hydrosulfite decomposition products.

In a large number of studies the optimum conditions of temperature, pH, retention time, consistency and the effect of metallic ions have been determined. Additives were found to reduce the effect of metal ions, thus increasing brightness by one or two points.

CHEMISTRY OF HYDROSULPHITE BLEACHING

Zinc and sodium hydrosulphite are used in the U.S. and Europe. Both are purchased as powders which are readily dissolved in cold water. Zinc hydrosulphite can also be prepared, from zinc powder and sulphur dioxide, ($\text{Zn} + 2\text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{ZnS}_2\text{O}_4 + 2\text{H}_2\text{O} + \text{heat}$) at the mill sometimes at a lower price than sodium hydrosulphite (10). The use of zinc or sodium hydrosulphite depends upon wood species and bleaching conditions.

As a result of instability of hydrosulfite it is usually prepared immediately before use.

Hydrosulfites hydrolyzes as follows (12) (all apply to $\text{ZN S}_2\text{O}_4$ and $\text{Na}_2\text{S}_2\text{O}_4$).

1. $\text{S}_2\text{O}_4^{-2} + 2\text{H}_2\text{O} \rightarrow 2\text{HSO}_3^{-1} + 2\text{H}^+$
2. $\text{S}_2\text{O}_4^{-2} + 2\text{H}_2\text{O} \rightarrow \text{S}_2\text{O}_6^{-2} + 4\text{H}^+$
3. $\text{S}_2\text{O}_4^{-2} + 3\text{H}_2\text{O} \rightarrow \text{HSO}_3^{-1} + \text{HSO}_4^{-1} + 4\text{H}^+$
4. $\text{S}_2\text{O}_4^{-2} + 4\text{H}_2\text{O} \rightarrow 2\text{HSO}_3^{-1} + 6\text{H}^+$
5. $2\text{S}_2\text{O}_4 + \text{H}_2\text{O} \rightarrow \text{S}_2\text{O}_3^{-2} + 2\text{HSO}_3^{-1}$
6. $\text{S}_2\text{O}_4^{-2} + \text{H}_2\text{O} + \text{O}_2 \rightarrow \text{HSO}_3^{-1} + \text{HSO}_4^{-1}$

The hydrogen released in formulas 1 to 4 reacts with pulp and reduces color components to a substance of lower color intensity. However, if free oxygen is present in the system the hydrogen will be oxidized before it can react with the pulp (formula 6). Because of this air entrapped in pulp

slurry is to be avoided. Formula 5 shows an auto-oxidation/reduction which also uses up bleaching chemicals and is to be avoided.

HYDROSULPHITE BLEACHING TECHNOLOGY

Some of the most critical rules for using hydrosulphites are:

- (1) the chemical should be prepared as close as possible to the point of use,
- (2) it should be mixed with pulp quickly, uniformly, and without aeration,
- (3) the pH for zinc hydrosulphite should be between 4.5 and 6, while for sodium hydrosulphite a pH of between 5 and 7 should be used,
- (4) the temperature should be between 140 and 170°F.

Type of Hydrosulfite

A comparison of zinc or sodium hydrosulfite should be made on the basis of material to be bleached and expense of chemicals. Zinc hydrosulfite may be cheaper because of on site manufacture (3). The zinc salt is also a bit more stable than the sodium salt. Bleaching action is, however, essentially the same for both salts and depends upon concentration.

Chemical Concentration

Increasing the concentration of hydrosulfite will give increased brightness. A point is reached at about 2% beyond which, although brightness increases, large increases in chemical concentration yield small gains in brightness (2, 3) or in one case (11) it was noted that increases above 2% sodium hydrosulfite on pulp actually caused a decrease

in brightness.

For bleaching groundwood concentrations are from 0.2 to 2.0% on bone dry pulp. Besides not increasing brightness much, if at all, large concentrations of hydrosulfite may cause serious corrosion problems.

Pulp Consistency

In the complete absence of air (displaced by nitrogen) it was found that consistency had no effect on brightness gain. At consistencies of between 5 and 12% with 1% $\text{Na}_2\text{S}_2\text{O}_4$ and 0.6% $\text{Na}_5\text{P}_3\text{O}_{10}$ the same brightness level of 70 C.E. was reached (11). In the presents of air, however, increasing consistencies decreases brightness, all other variables were held constant. The reason for this seems to be that at higher consistencies there are more voids and a larger over-all surface area favoring reaction with oxygen.

Temperature

In general the effect of higher temperature is to reduce retention time and raise the maximum brightness. The range most commonly used is between 110 and 170°F. It has been reported that temperatures up to 230°F can be used with hydrosulfite stabilized with polyphosphate or with an organic chelating agent (2).

Increasing temperature up to 170°F seems to promote the reduction of

of groundwood color producing groups more than the decomposition of hydrosulfites (12). Above 170°F the beneficial effects of high temperature seem to be offset by a decrease in hydrosulphite stability and an increase in groundwood darkening.

Retention Time

In reviewing several sources (2, 10, 12) there was a general agreement that one hour was the most commonly used retention time as at lower temperatures (approx. 110°F) 90% of the total brightness gain can be obtained. Raising the temperature decreases the time to achieve 90% of brightness gain, a period of 30 to 45 minutes was found adequate at temperatures between 140 and 165°F. Hydrosulphite bleaching is fast and in general 75% of the total brightness gain is obtained in the first 5 to 10 minutes.

pH

One should separate the effect of pH on groundwood from the effect of pH on the bleaching process.

Increasing the pH of a groundwood slurry decreases brightness. This could be the result of either the formation of free radicals or a shift in the absorption spectrum of lignin caused by salt formation of phenolic hydroxyl groups involved in the lignin chromophores (12). Increasing temperature increases the effect of alkalinity because of demethylation

and oxidation of quaiacyl groups present in lignin (12).

The effect of pH on hydrosulphite is different. For the temperature range between 110 to 170°F the peak brightness for either sodium or zinc-hydrosulphite occurred at a pH of just over 5. The brightness values drop off rapidly above pH 7. This drop in brightness in the alkaline range is general for groundwood heated over 110°F. It is likely that the maximum brightness occurs near pH 5 for the following reasons:

"1. The decrease in brightness on the acid side is due to the decomposition of hydrosulphite; 2. The drop in brightness on the alkaline side may be due to the formation of new lignin chromophous when the groundwood is heated, or to decreased reactivity of the existing chromophores in alkaline medium or both" (12).

This would explain why using hydrosulphite in an alkaline medium where it is more stable and reductive causes the groundwood to darken. Above pH 10 there are more chromophores produced by alkali action than there are chromophores reduced at any level of hydrosulphite addition.

The optimum pH range for zinc hydrosulphite is between 4.5 and 6, while for sodium hydrosulphite a pH of between 5 and 7 gives the best results. But, the particular pH level used is the result of a number of factors - pitch control, wood species, and pH and chemical composition of process water.

During the bleaching process the pH will drop between 0.3 to 1.0 pH

units depending upon level of treatment water used, and temperature . In general, the greater the degree of aeration the lower the pH becomes as a result of the formation of sulfuric acid, thiosulfuric acid, and sulfurous acid (2).

Oxygen

As seen by the reaction $S_2O_4^{-2} + O_2 + H_2O \rightarrow HSO_3^{-1} + HSO_4^{-1}$ oxygen in the presents of hydrosulphite causes decomposition to occur. Back (11) found that to bleach to a given brightness level in the presents of increasing amounts of oxygen demanded greater amounts of hydrosulphite than would be required on a strictly theoretical basis. The decomposition of hydrosulphite due to oxygen increases faster than the oxygen increase (11, 12,). The reason for this decomposition was explained by Back (11) in this way:

"Chemical reactions of hydrosulphite are complex. Bisulphite, a decomposition product of hydrosulphite by oxygen could cause hydrosulphite to decompose further into thiosulphate, pyrosulphite, hydrogen sulphite, elemental sulphur, and a whole gamut of sulphur compounds. It is possible that the reduction in brightness could be due to the elemental sulphur being able to combine with lignin to form colored sulphur lignin of compounds".

In order to minimize the effect of oxygen, in a mill situation, it is good to bleach at low consistency as there is less air in stock, deareate .

stock with steam, mix hydrosulphite and stock quickly (less than 4 minutes) (13) and thoroughly in the absence of air, and do not expose stock to air until retention time is completed. In an experimental situation bleaching in the absence of air is usually done under a nitrogen atmosphere.

Sequestering Agents

According to Gupta and Mutton (9) one of the greatest difficulties with hydrosulphites is their instability and decomposition during bleaching. The decomposition is believed to be catalyzed by metal ions present in pulp and water although there is no direct experimental evidence to support this. In order to stabilize hydrosulphites a chelating agent is used, or at least recommended, such as sodium tripolyphosphate (STPP) or ethylenediaminetetraacetic acid (EDTA). When bleaching with zinc hydrosulphite the effects of a chelating agent are said to be marginal, however, the use of STPP or EDTA are well established in the industry.

In practice STPP is the more commonly used of the two. Its treatment level is approximately 0.5% on pulp.

Washing

Washing of hydrosulphite bleached pulp is done in some mills to reduce the effect of corrosion on wire and felt life.

A problem with washing seems to be rapid reversion of brightness

during storage (2) for the first 6 to 12 hours. Unwashed pulp may increase in brightness slightly during storage for the first 6 to 12 hours. Reversion of washed pulp was attributed to the loss of residual hydrosulphite which acts to protect the pulp.

Brightness Reversion

The brightening effect of hydrosulphite will gradually disappear during storage but the normal rate is difficult to determine (10) since it depends upon bleaching conditions, storage conditions, and chemicals added. Reversion can be slowed down by using a chelating agent, bleaching at the lowest possible pH (12), or sprinkling bleached pulp with a solution of bisulphite. Of the three only bleaching at a low pH will slow reversion due to sunlight. For the others, two to three hours of sunlight is enough to bring brightness down several points below the original level of unbleached pulp and only two points above similarly exposed unbleached pulp.

The difference in brightness after exposure to sunlight, between bleached and unbleached pulp may be explained by assuming that there are two groups of chromophores in the groundwood (12). One group is responsible for the difference in brightness after reversion (2 to 3 points) and its effect is permanent. The other group is responsible for a large increase in brightness (up to 10 points) on bleaching but is easily reoxidized to the colored form during reversion treatment.

TWO-STAGE PEROXIDE-HYDROSULPHITE BLEACHING

Because peroxides are oxidizing agents and hydrosulphites are reducing agents one could assume that they react differently with pulp and using them both yields a brighter pulp than either one alone. This is the case, their effects, within limits, are additive. If a certain pulp has a brightness increase of 14 points using peroxide alone or an increase of 12 points using hydrosulphites alone the effect of two-stage peroxide-hydrosulphite would be between 18 and 22 points increase (3, 14, 15).

The order of bleaching is important. Hydrosulphite followed by peroxide yields a poorer brightness gain than peroxide alone because the peroxide reoxidizes whatever the hydrosulphite has reduced (3, 14, 15). The opposite sequence, peroxide followed by hydrosulphite, gives the additive brightness mentioned in the above paragraph.

All procedures for maximum brightness gain, followed when bleaching with either chemical, are followed when bleaching in a two-stage process. It is recommended that SO_2 be used between stages to neutralize residual peroxide and also as a pretreatment for the hydrosulphite stage.

OBJECTIVE

To use existing technology for bleaching with peroxide and hydrosulphite to bleach groundwood over 80 G.E. points. A two-step peroxide-hydrosulphite sequence will be used to achieve desired brightness level. A high brightness is necessary in order to extend the uses of groundwood in manufacturing paper.

EXPERIMENTAL SECTION

EQUIPMENT AND PULP CONSIDERATIONS

Bleaching with H_2O_2 presents few equipment problems as it is an oxidizing agent and is not affected by oxygen in air. It is however, reduced in strength by heavy metals (which act as catalyst) or dust therefore distilled water must be used and burets flushed with H_2O_2 prior to use.

Hydrosulphite is a reducing agent and is therefore oxidized quickly and easily by the oxygen in air. An apparatus was assembled (see Figure 10) which, after being purged with nitrogen allowed hydrosulphite to be mixed, drawn into a self-filling buret and added to pulp slurry without exposure to air.

The pulp bleached was spruce groundwood. After conditioning was stored in an opaque, covered plastic container in the same room it was conditioned. The unbleached brightness was found to be 45 G.E. points.

EXPERIMENTAL CONDITIONS

For hydrogen peroxide conditions were varied as follows:

1. 12 gm OD sample of pulp, 112°F, 5% consistency, 0.5% EDTA, 5% Na_2SiO_2 , pH 10.5 adjusted with NaOH, H_2O_2 was varied from 0.5 to 3.0% in 0.5% steps.
2. Above conditions were the same except pH was adjusted with Na_2CO_3 and H_2O_2 was varied from 1.0 to 6.0% in 1.0% steps.
3. 0.01N HCl extraction replaced EDTA to remove heavy metals and consistency was raised to 12% than 18%.

For zinc- or sodium hydrosulphite condition were as follows:

1. 12g OD sample, 0.01 N HCl extraction, 136°F, 3% consistency, 5% Na_2SiO_2 , pH 7.0 adjusted with SO_2 .

For combination bleaching conditions were as follows:

1. 12g OD sample, 0.01N HCl extraction, 12% consistency, 5% Na_2SiO_2 , pH 10.5 adjusted with Na_2CO_3 , 3.0% H_2O_2 on pulp for 3 hours at 117°F. Next, dilution to 3.0% consistency with distilled H_2O , soaring to pH 7 with SO_2 , bleaching with $\text{Zn S}_2\text{O}_4$ or $\text{Na}_2\text{S}_2\text{O}_4$ at 0.5 to 3.0% levels of addition in 0.5% steps, 136°F 2 hours retention.
2. Above conditions the same except consistency during H_2O_2 stage was 18%.

The formation of handsheets was done as follows: dilution of slurry to 0.5% consistency, souring to pH 4.5 with SO₂, filtering through Buchner Funnel, pressing between blotter paper and British Sheet Mold disk and allowing pad to air dry. Brightness readings were taken on the side of the pad exposed to air during filtering.

OBSERVATIONS

Bleaching at lower consistencies, 3.0 to 5.0%, is relatively easy as pulp slurry is easily mixed and beakers can be used. Above 5.0% consistency automatic mixing becomes extremely difficult and plastic bags had to be used. At consistencies between 12.0 and 18% the pulp looks slightly damp and additions of small amounts of peroxide (from a 30% solution) are not readily dispersed throughout the sample.

Of the three bleaching agents peroxide gave the most obvious increase in brightness. Brightness increase appeared gradually over the two hour bleaching cycle with three hours being the practical limit. Peroxide also seemed to produce a cleaner pulp which was smoother upon being made into a handsheet.

Hydrosulphite, though difficult to work with because of the nitrogen atmosphere, was extremely fast acting. The brightness of the slurry could be seen to increase as bleaching agent was being added (for pulps not pretreated with H_2O_2). For samples pretreated with peroxide the addition of hydrosulphite visually did little for pulp brightness.

DISCUSSION OF GRAPHS

The use of NaOH to adjust the pH of slurries to be bleached with peroxide (Figure 1) lead to significantly darker pulps then using Na_2CO_3 (Figure 2) as a combination base-buffer. It would seem as though the NaOH would be contributing to the browning reaction causing the peroxide more work.

Using hydrogen peroxide at lower consistencies with EDTA as a chelating agent gives a brightness rise of approximately 15 points at a 3% level of addition (Figure 2). Compare this with zinc hydrosulphite (Figure 5) that gave an 8.7 point rise in brightness or sodium hydro-sulphite that gave an 11 point rise (Figure 6), both at a 3% level of addition, and it can be readily seen that peroxide is the better of the three for brightness increases. This is true at any level of addition.

An HCl extraction was optimized (Figure 3, Figure 4) and found to be 0.01 N. Less than this does little to aid the removal of heavy metals. Concentrations above 0.01 N must react with lignin and begin its degradation because brightness falls off rapidly and levels off at approximately 56 G.E. points (Figure 3).

Comparing the use of EDTA (Figure 2) as a chelating agent with an HCl extraction (Figure 4) yields no great difference in obtainable brightness at a 3% level of H_2O_2 addition. Although the HCl extraction provided pulp that was slightly higher in brightness 1.7 G.E.point, the consistency and temperature were also higher which would favor a brightness increase.

As I had been told that people met with difficulty in the past using EDTA I decided to be safe and use an HCl extraction throughout.

The effect of increasing consistency on peroxide bleaching is readily seen when comparing Figure 7, bleached at 12% consistency, and Figure 8 bleached at 18% consistency. The difference in the peroxide stage of bleaching is over 6 points in favor of the higher consistency.

The effects of sodium or zinc hydrosulphite are the same when used in a two-stage process. The zinc salt raised brightness 3.4 points at a 2% level of addition (Figure 8) while the sodium salt increased brightness three points (Figure 9). The difference could be accounted for due to sheet roughness.

When used alone the sodium salt was found to be superior by over two points. The difference between the two could be explained because the sodium salt had a greater quantity of free SO_3 , 0.0256 g/ml, than did the zinc salt, 0.023 g/ml.

If the effects of hydrogen peroxide and sodium or zinc hydrosulphite were additive I could expect a maximum brightness rise of 33.2 points. As it turned out the best I could do is a 26 point increase. This is probably because the hydrosulphite tends to reduce a small amount of color producing groups the peroxide had oxidized.

The 71 point level I reached was far short of the 85 level I was shooting for however, a 26 point increase isn't bad. It would seem logical that if high brightness levels are desired a pulp of high initial brightness should be used.

SUGGESTIONS FOR FURTHER STUDY

As the starting material is extremely important to the final product, I would suggest obtaining pulp samples of known origin. Freshly pulped samples of a material low in extraneous compounds (such as poplar) would be recommended.

Also, the formation of pads with a Buchner Funnel isn't such a good way of doing it. They tend to be rough in some areas and smooth in others, I suggest the use of the Noble and Wood machine as follows: form the sheet, press it, remove it from the screen, place a British Sheet Mold disc in the center and cut around it, press sample between blotter paper and air dry. This would yield a much smoother sheet from which to take brightness readings.

CONCLUSION

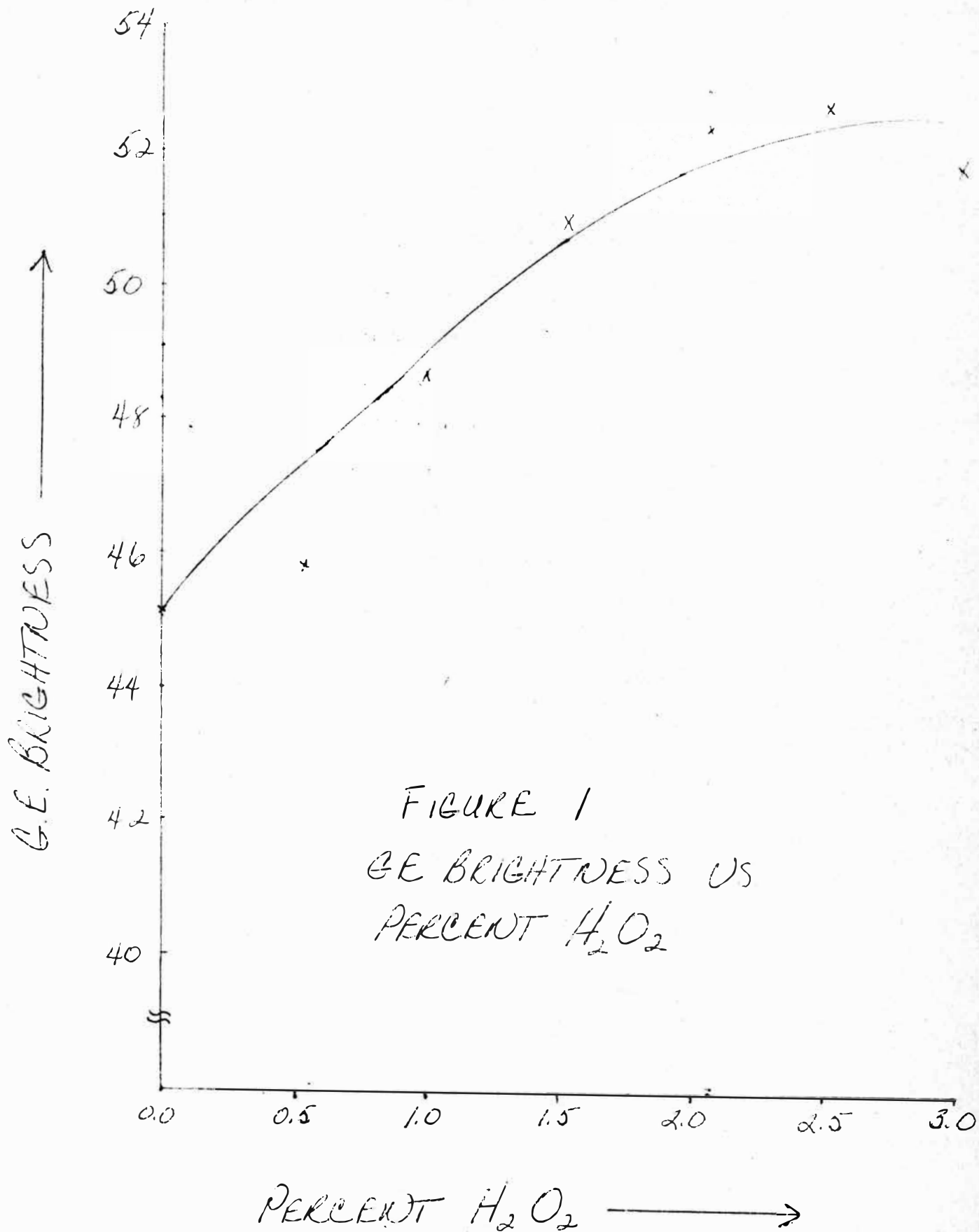
Peroxide is by far the workhorse in so far as brightness rise is concerned. It is easy to work with and provides a clean bright pulp with a brightness increase in the order of 15 to 20 points at levels of addition of approximately 2.0%.

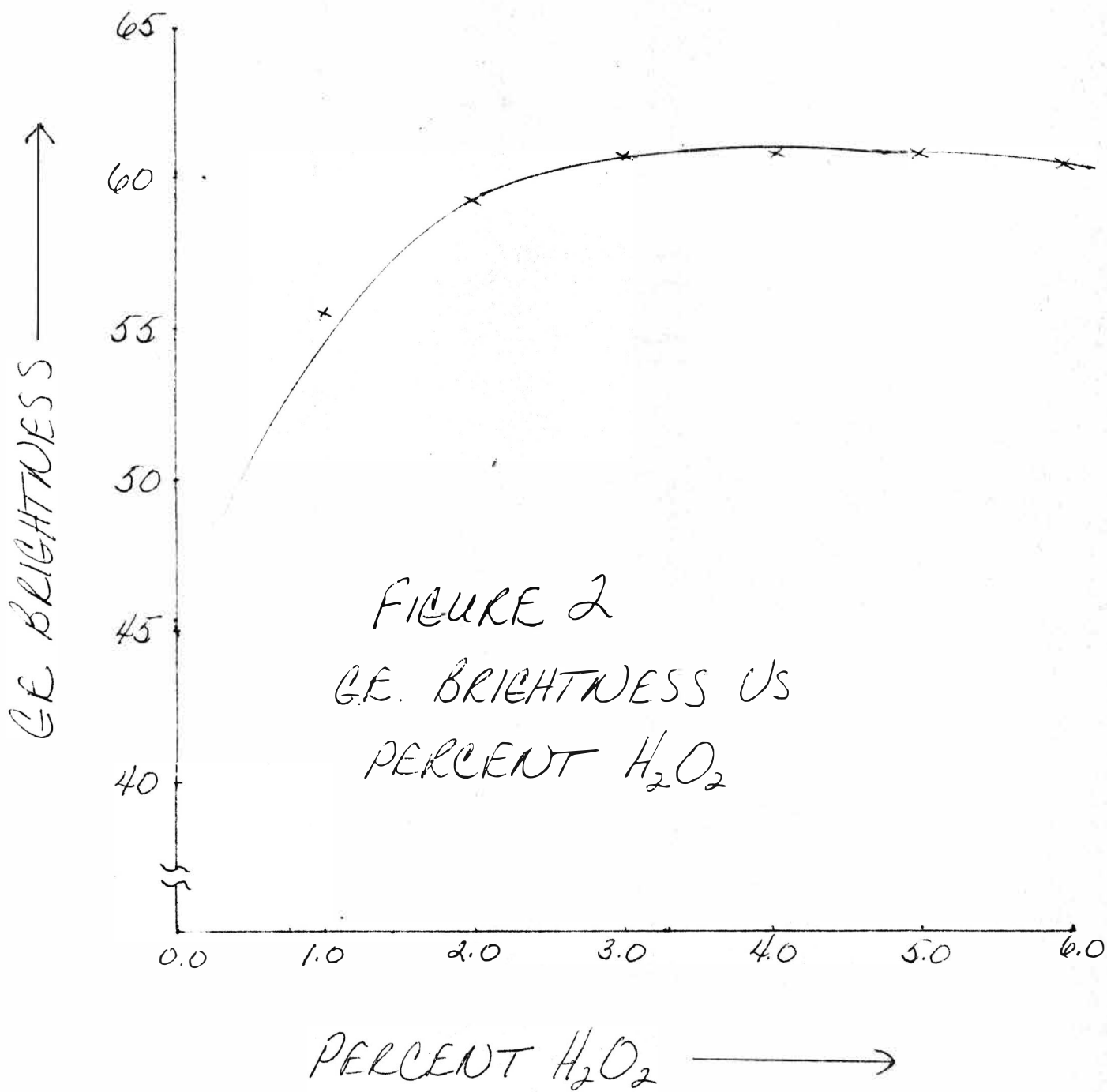
Hydrosulphites are rapid acting reducing agents capable of increasing brightness in the order of 8 to 10 points at lower levels of addition, approximately 2.0%. Above the 2.0% level actually caused brightness decreases when used alone. Hydrosulphites are more difficult to work with on a laboratory, then are peroxides, as a result of their rapid oxidation by air. Between the sodium and zinc salts, sodium seems to do a slightly better job of raising pulp brightness when used in a single stage.

When combining the brightening powers of peroxide and hydrosulphite in a two-stage process the resulting pulp approaches, but never reaches, a totally additive effect of the two individual brightness gains. There was no observed difference between sodium or zinc hydrosulphite when used as the second stage.

The use of an HCl extraction to remove heavy metal is an effective method, however, under test condition, it was no more effective than EDTA.

The end brightness of a pulp sample would seem to be dependent upon the initial brightness as much as the conditions under which it is treated. To treat a pulp with peroxide and hydrosulphite and achieve over 80 brightness without rendering lignin soluble and decreasing yield, requires a starting material of high initial brightness.





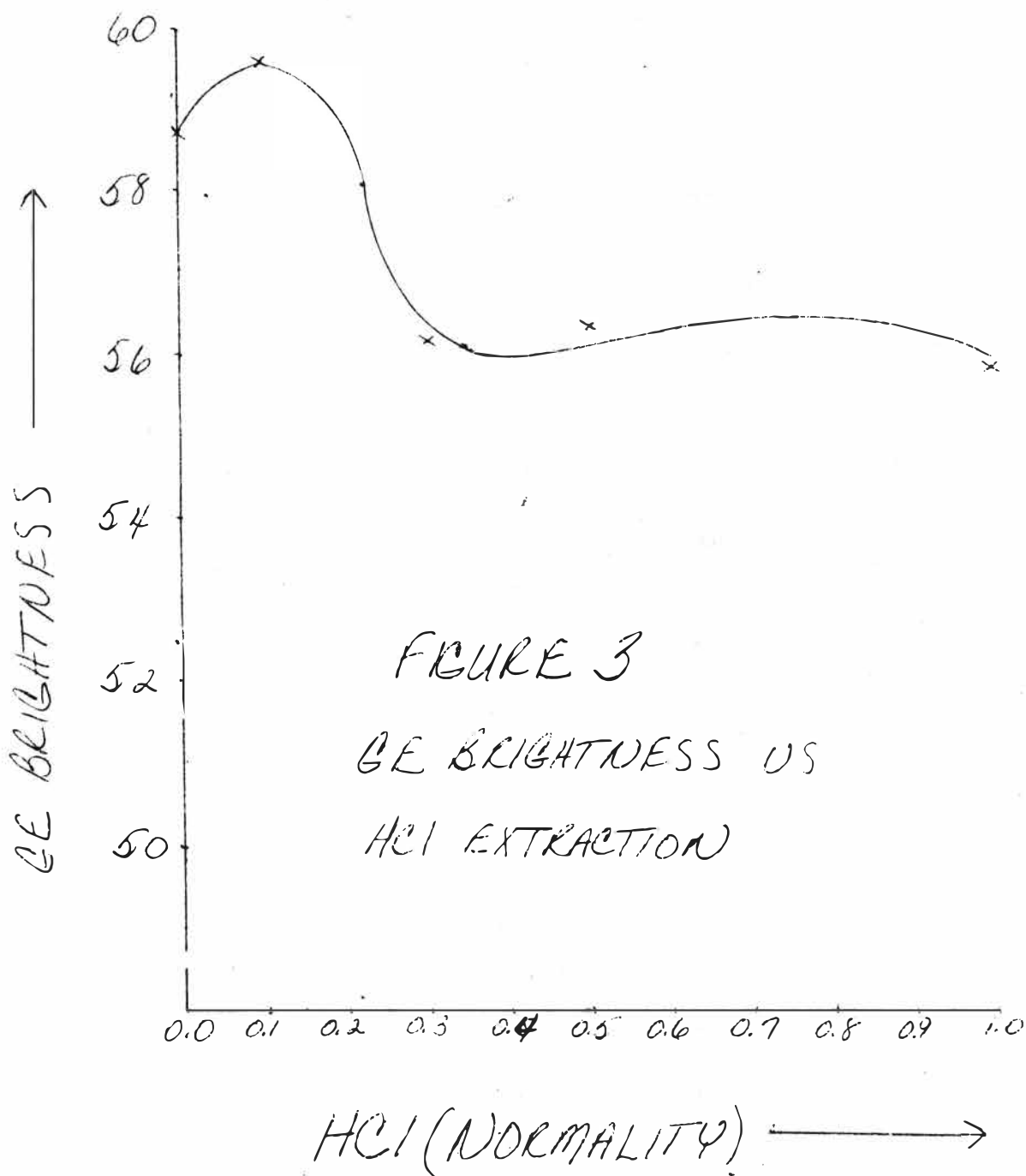


FIGURE 4
GE BRIGHTNESS VS
HCl EXTRACTION

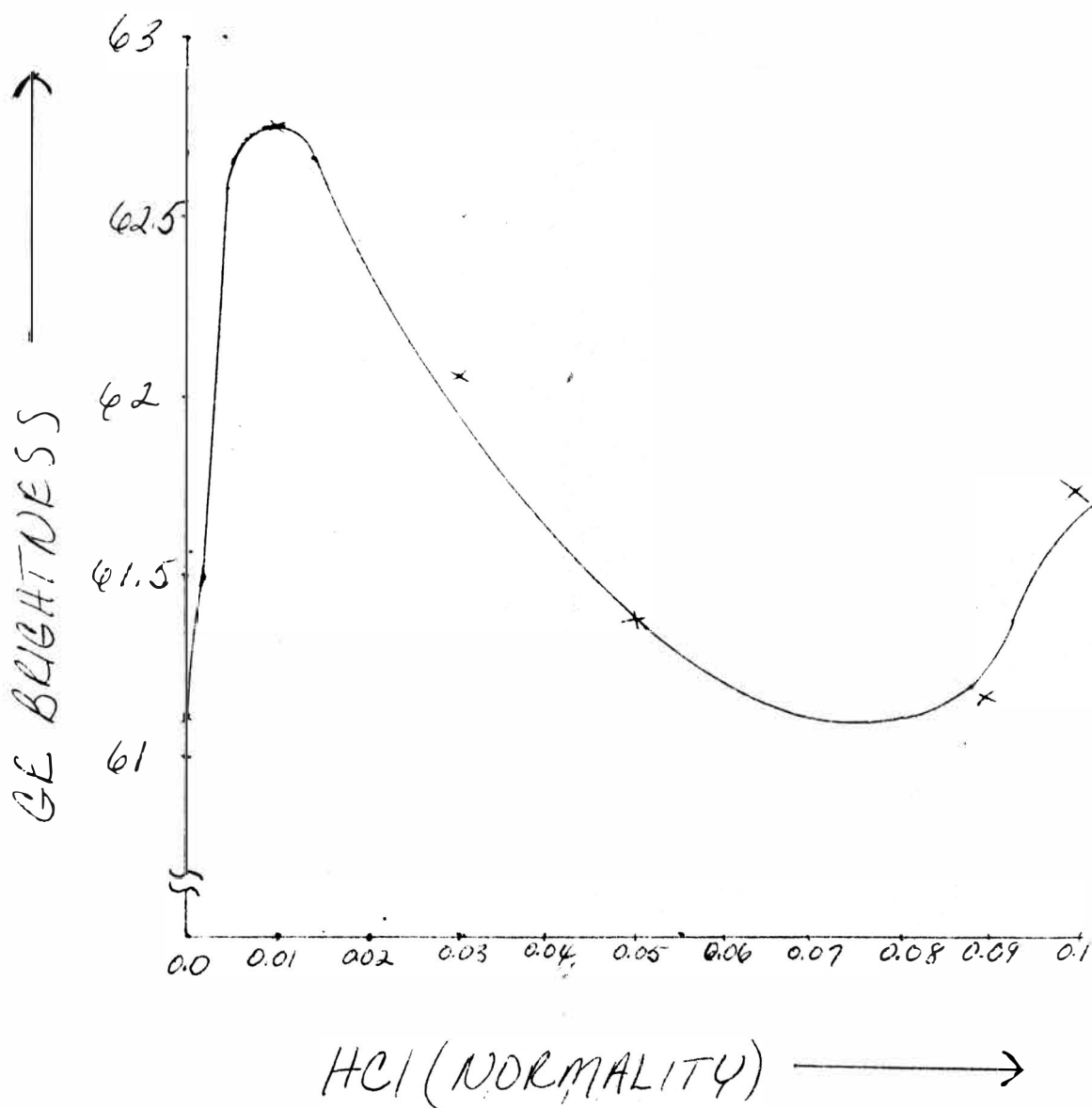


FIGURE 5
GE BRIGHTNESS VS
PERCENT ZnS_2O_4

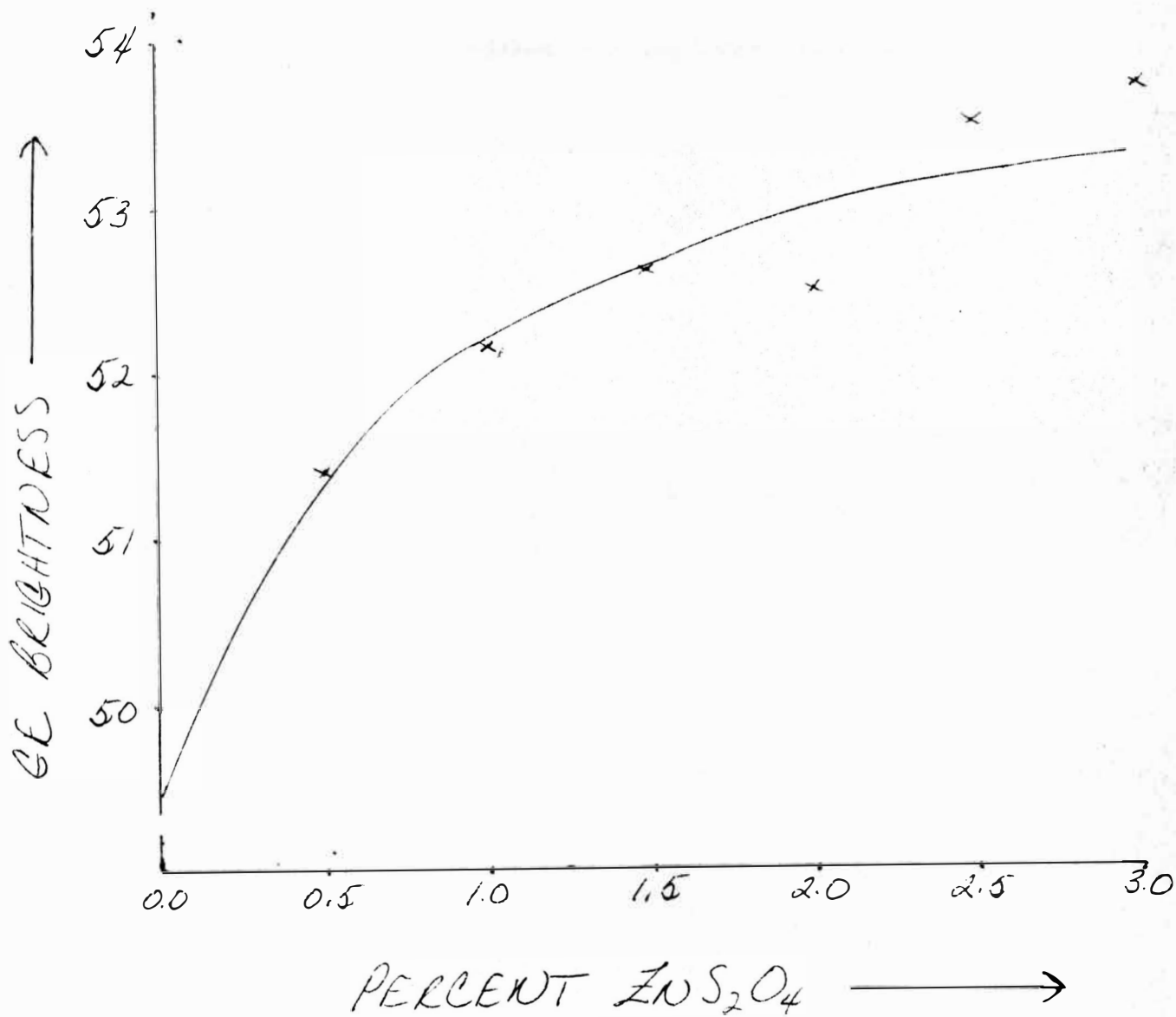
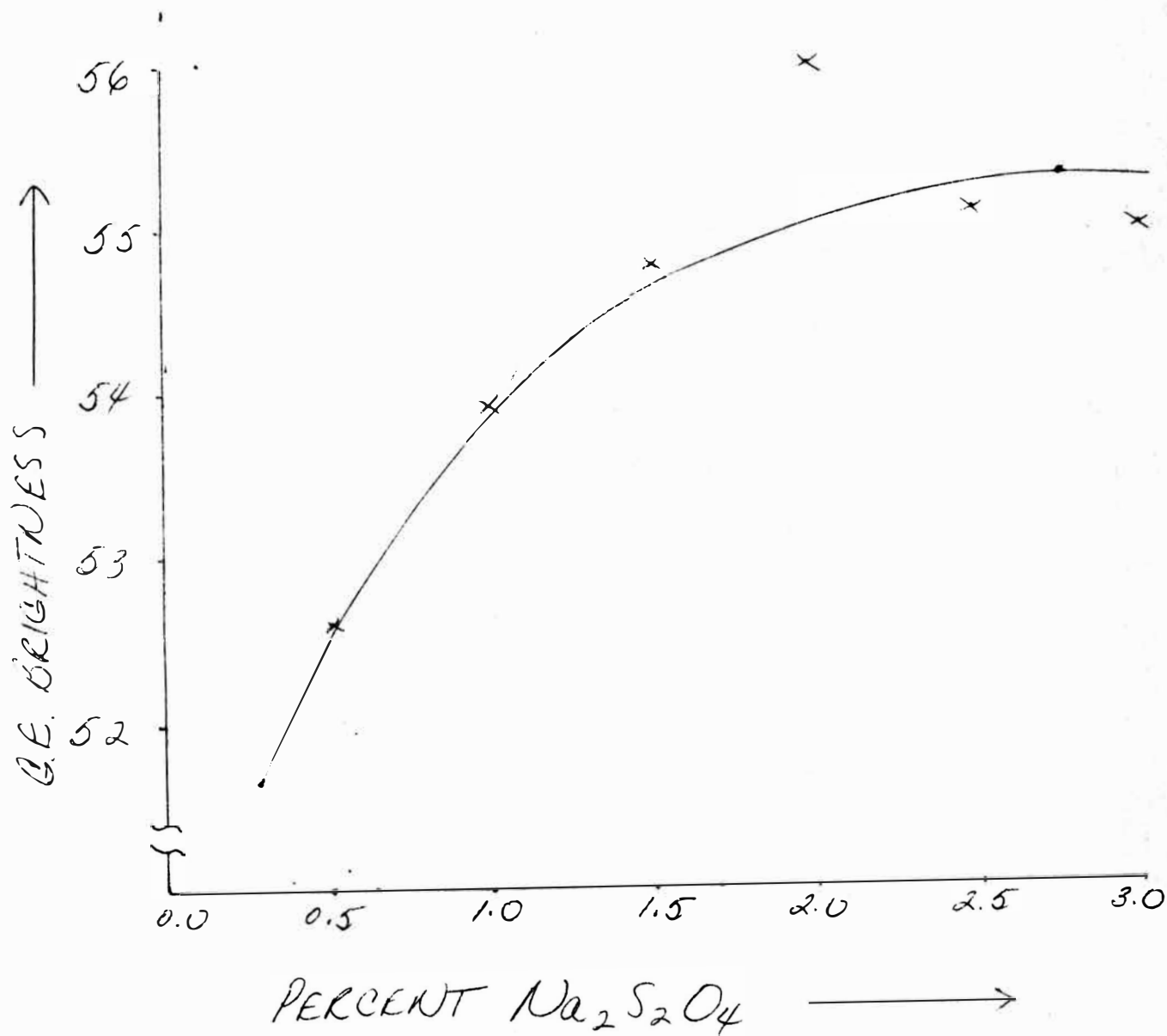


FIGURE 6
G.E. BRIGHTNESS VS
PERCENT $\text{Na}_2\text{S}_2\text{O}_4$



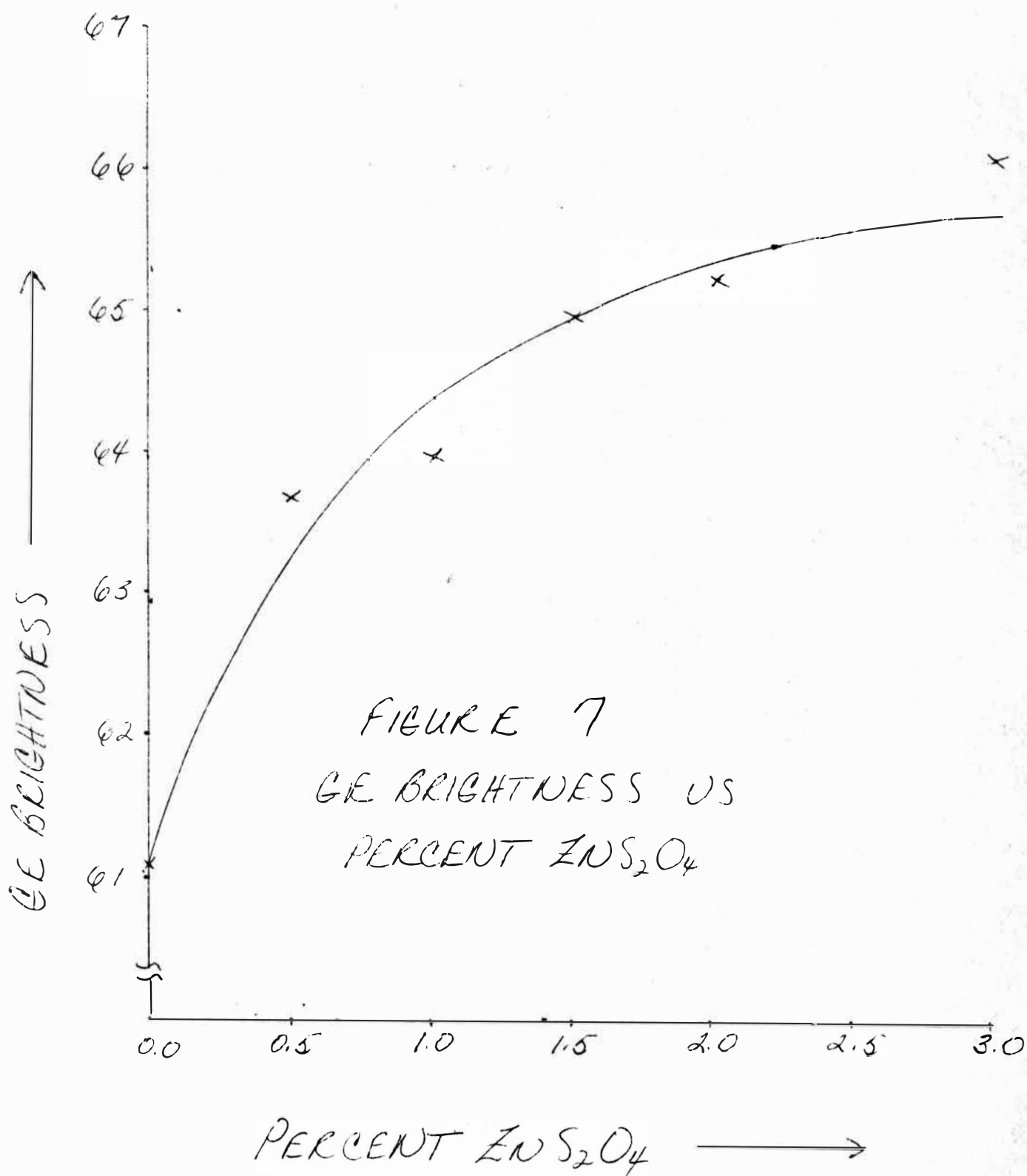


FIGURE 8
GE BRIGHTNESS VS
PERCENT ZnS_2O_4

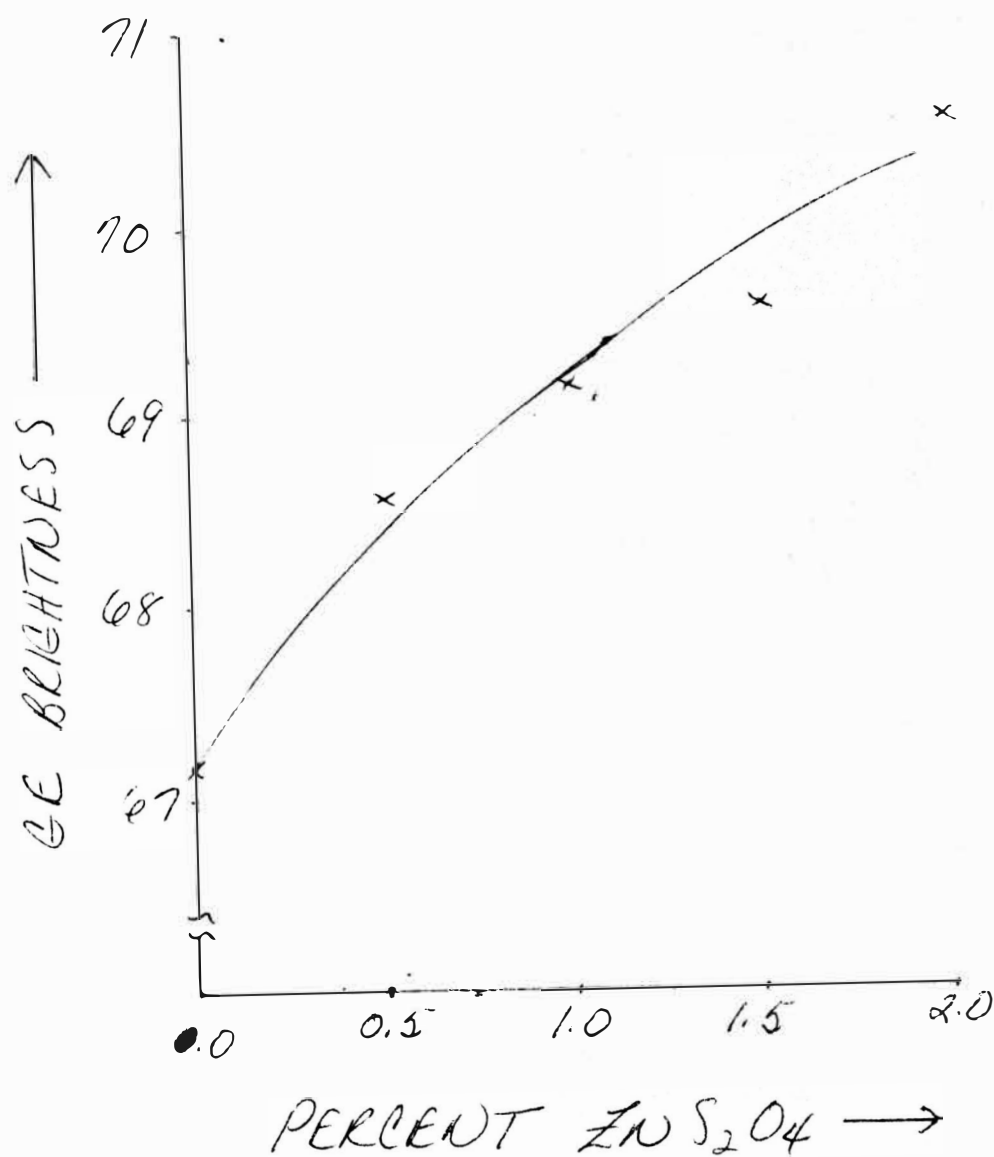
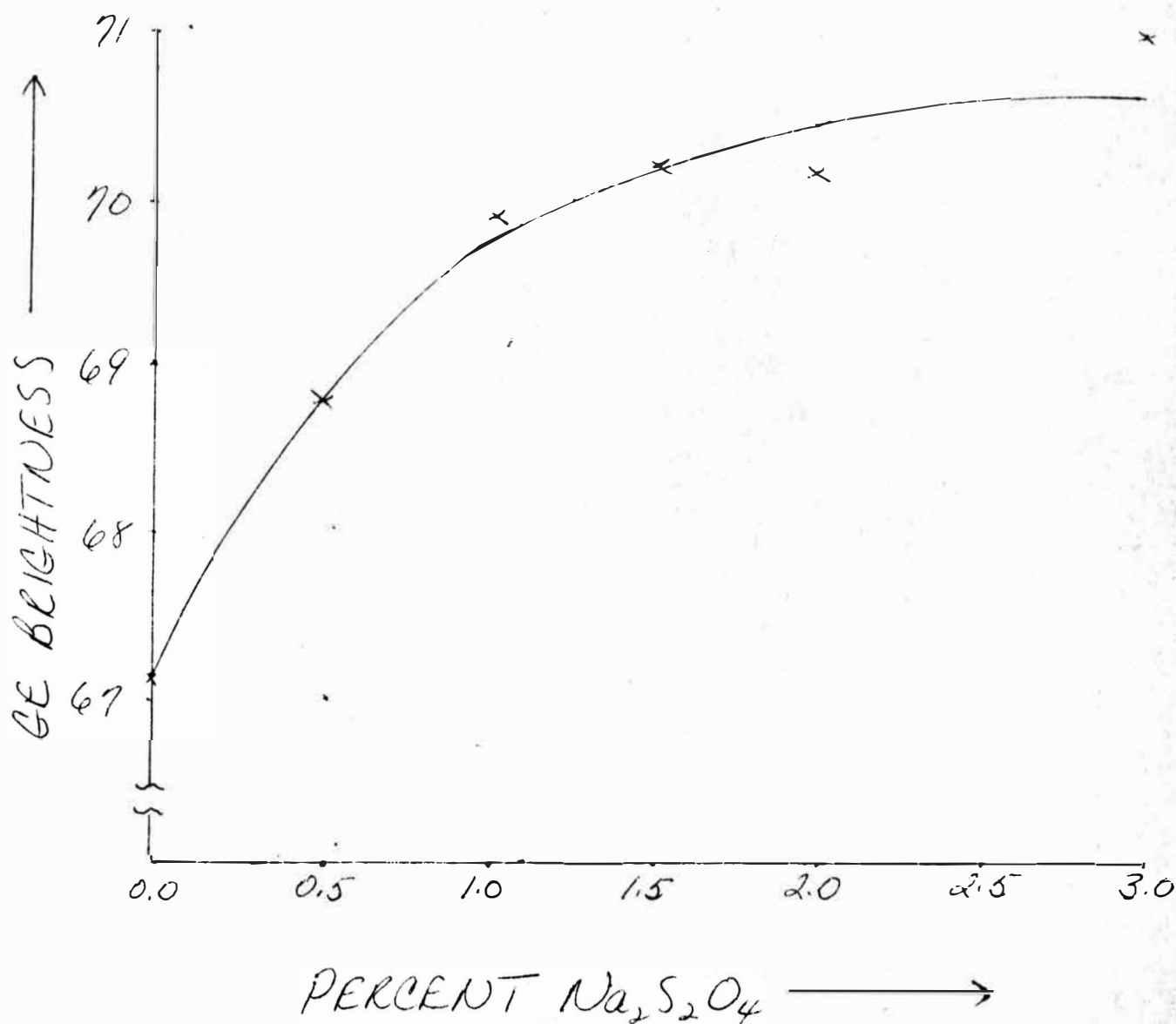


FIGURE 9
GE BRIGHTNESS VS
PERCENT $\text{Na}_2\text{S}_2\text{O}_4$



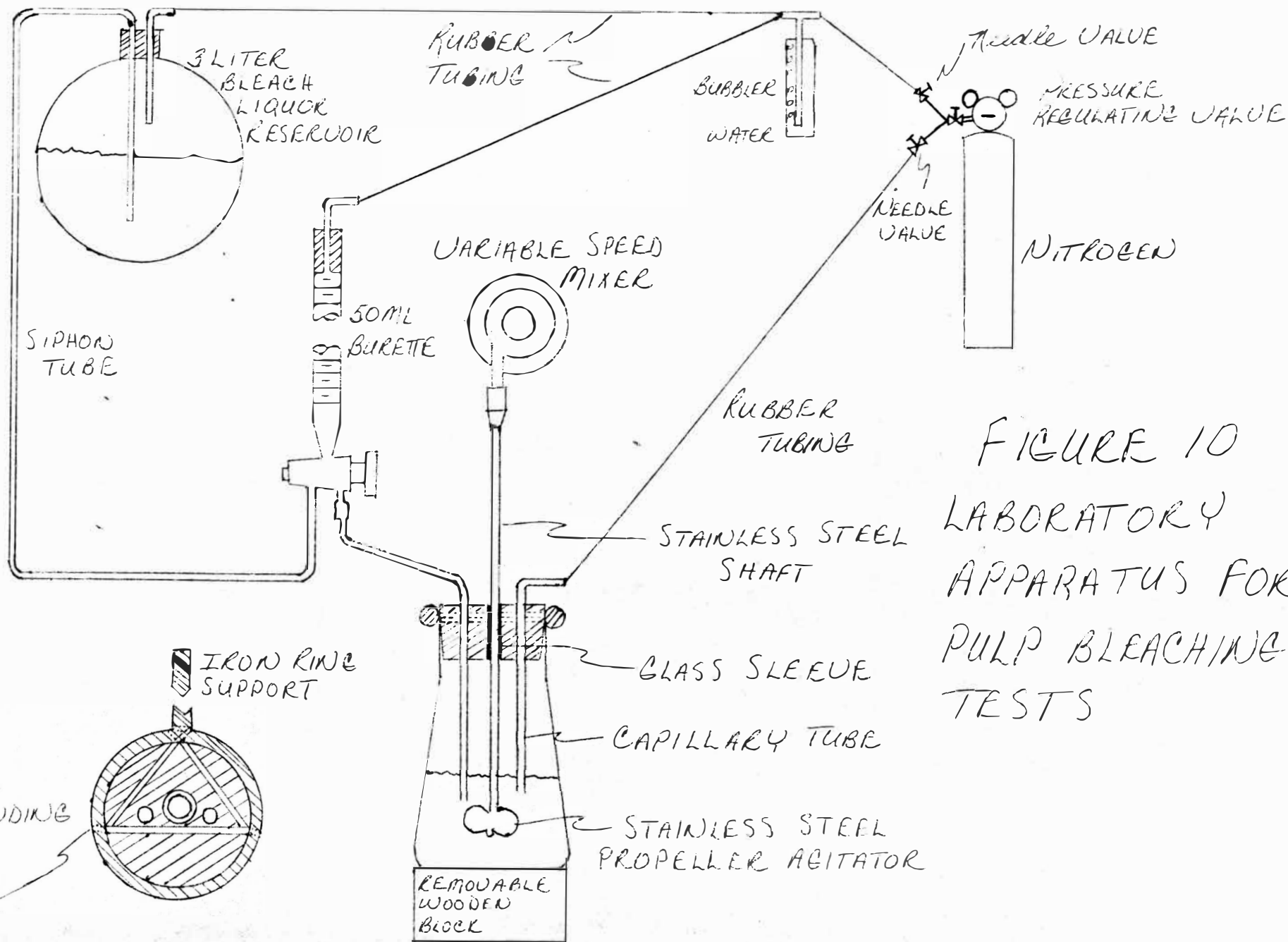


FIGURE 10
LABORATORY
APPARATUS FOR
PULP BLEACHING
TESTS

BIBLIOGRAPHY

1. TAPPI Monograph No. 10, pg. 210-277.
2. TAPPI Monograph No. 27, pg. 199-216.
3. Andrews, D. H., Pulp and Paper Magazine of Canada (June 7, 1968).
4. Stove, M.L., Tappi 48, No. 9: 535-4, (September, 1965).
5. Gupta, V.N.; Mutton, D.B., Pulp and Paper Magazine of Canada 70, No. 11: 77-84, (June 6, 1969).
6. McEwen, R.L., Paper Trade Journal, (November 14, 1952).
7. Rapson, W. H., Wayman, M. Anderson, C.B., Pulp and Paper Magazine of Canada 66, No. 5, T225-7, (may, 1965).
8. Fennell, Tappi 43, No. 11; p 903, (November, 1960).
9. Gupta, U.N.; Mutton, D.B., Pulp and Paper Magazine of Canada 70, No. 11: 77-74 , (June 6, 1969).
10. Gavelin, G. Paper Trade Journal 150, No1. 26:42-6, (June 27, 1966).
11. Back, S., Tappi 39, No. 4: p. 170A, (April, 1956).
12. Tyminski, A., Pulp and Paper Magazine of Canada, No. 6, (June 1967).
13. Barton, R.W., Tappi 44, No. 8, p 161A, (August, 1961).
14. Barton, R.W., Tappi 41, No. 3, p. 161A (March, 1958).
15. Witkowski, C.J., Paper Trade Journal, 156, No. 23: p. 25, (May 29, 1972).