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## Doctor's Dissertation

**A Study of the Chemical Recovery in the Monosulfite Pulping Process**

**by Frederick B. Schelhorn**

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# A STUDY OF THE CHEMICAL RECOVERY IN THE MONOSULFITE PULPING PROCESS

A thesis submitted by

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# INTRODUCTION

## NEUTRAL SULFITE PROCESS

Although the earliest use of sodium monosulfite (commonly designated as neutral sodium sulfite) for the production of cellulose from naturally occurring materials is somewhat obscure, Cross (1) in 1880 referred to it as one of four pulping methods and in the same year was granted a patent (1a) in which he disclosed the complete process. Pulping was then considered to be a process by which the natural lignocellulose was hydrolyzed and the components prevented from recombination by fixing the reactive groups of the lignin in chemical combination with the pulping agent. These reactive groups were thought to be acidic and aldehydic; consequently, the sodium sulfite should possess excellent pulping qualities because the base could combine with the acidic groups of the lignin, whereas the sulfite residue would be free to react with the aldehydic groups. It was found, however, that sodium sulfite was a weak pulping agent and required increased temperature and concentration to effect successful digestion. Cross attributed this fact to the feeble hydrolyzing power of the salts and suggested the use of temperatures in the range of 160-180° C. to increase the reaction velocity.

The process was given its earliest commercial impetus by Schacht (2) who patented a process utilizing monosulfite in the pulping of straw and claimed several advantages over the common pulping methods. Increased yields of 15 to 20 per cent over the bisulfite method were obtained, and the objectionable odors associated with the alkaline

process were eliminated. Schacht prepared the cooking liquor by passing sulfur dioxide into a crude soda solution until the latter was nearly saturated. The residual carbonate present was then causticized with lime to yield caustic soda. This residue of free caustic was needed to solubilize silicate and alumina found as inherent components of the raw material (straw), and it was suggested that it be kept as low as would be conducive to successful operation. This process was evidently tested on a commercial scale, but soon fell into disuse because of its faulty recovery system with resultant high raw material cost.

Sodium monosulfite was first employed in the pulping of wood by Drewsen (3), who patented a process for its utilization in the preliminary penetration of chips which were to be subsequently pulped by the bisulfite process. The main objects claimed for this process were the elimination of the offensive odor and the extremely corrosive action on the digester by the bisulfite solution and, at the same time, an improvement in the penetration of the liquor into the chip so that burning would be prevented. Drewsen (4) further patented the application of the neutral sulfite process to the pulping of cornstalks, bagasse, and straw, and also claimed priority (5) for the cooking of wood (poplar) by this method (which was carried out as early as 1914), although the process was never patented.

During the decade following the last war, considerable interest was aroused in the possible commercial application of sodium monosulfite in the production of wood pulp. One of the reasons for this was the fact that, at that time, the commercial bleaching of kraft pulp was not

feasible and there was a ready market for pulps of high physical strength which possessed high brightness and could be bleached by the existing methods. Neutral sulfite pulp is frequently characterized, especially in the sales literature, as having "the strength of kraft and the color of sulfite."

Applicability to a wide range of wood species and the use of iron digesters in the cooking process, because of the alkaline liquors, were other factors of economic and technical interest.

The Keebra process of Bradley and McKeefe, which was developed at about this same time, contributed to the general interest in the neutral sulfite process. The Keebra process (6) utilized, in addition to the monosulfite, regulated amounts of other sodium salts—namely, bisulfite, sulfide, hydroxide, thiosulfate, carbonate, or bicarbonate. These individual cooking methods were then known as Acid Keebra, Thiokeebra, Semikeebra, etc., and were all duly protected by a complex system of patents. The inventors claimed advantages in the pulping of aspen, as well as other deciduous and resinous woods. Subsequently, the monosulfite process was utilized in the pulping of shortleaf pine and Douglas fir by Chidester and McGovern (7, 8), and was further patented by Drewsen in its application to deciduous woods (9) and resinous woods (10). The method has been successfully utilized in the pulping of many straws and grasses (11); Bray and Peterson (12) used flax straw, Clark (13) employed esparto, and Hilpert, Wolter, and Hofmeister (14) used the neutral and alkaline sulfite processes for the digestion of esparto and winter wheat straw. Finally Horváth (15) further studied

the use of monosulfite in pulping cornstalks, and Lynch and Doss (16) found certain advantages in the production of bagasse cellulose.

Another very important growth of the neutral sulfite process has been in the field of semichemical pulping. Rue, Wells, Rawling, and Staidl (17) have worked out a process which included an impregnation with monosulfite, followed by cooking and subsequent mechanical disintegration. This process is now in commercial operation on extracted chestnut and other hardwoods for the production of the so-called semichemical pulps. The advantages of such a process are the low chemical consumption and high yield, and the pulp is suitable for medium and low-grade printing paper and board. Sodium sulfite is an excellent reagent for this method because of its ready solubility, neutrality, and reducing properties.

The effect of cooking variables in the pulping of black gum have been studied by Bray and Eastwood, who investigated the effect of the ratio of sulfite to bicarbonate on the pulp properties (13) and the effect of digester temperature on the rate of delignification (19). Rawling and Staidl (20), pulping aspen with neutral sulfite, found that materials other than lignin were not removed until a temperature of 170° C. was attained. This is in sharp contrast to the soda process, in which cellulose attack is initiated at 140° C. The results of Rawling and Staidl are in good agreement with the pulping temperatures originally stipulated by Cross.

RECOVERY PROCESS

Because of the high chemical concentration required for the successful application of sodium monosulfite to the pulping of fibrous materials, it is evident that a suitable process for the recovery of the pulping agent, particularly the sodium salts, is of primary importance if the process is to compete with other pulping processes. The ideal situation would be a completely closed cycle involving only the use of a small quantity of make-up chemical in the production of the fresh cooking liquor. This was the goal of Bradley and McKeefe who have proposed, in a series of patents, several possible methods of disposal of the Keebra waste liquor so that the valuable constituents could be readily recovered.

An early patent (21) by these inventors suggested sulfiting the waste liquor so that the organic materials are precipitated, with the production of a suitable cooking liquor which may be causticized if desired. Evidently the amount of organic matter removed in this way is rather small, because they further proposed that the liquor be concentrated and sodium sulfite be allowed to crystallize from the solution (22). Finally, gypsum is added to the neutral or alkaline solution. Calcium sulfite is precipitated with the formation of sodium sulfate, which can then be separated by further concentration and crystallization. The calcium sulfite is treated with sodium sulfate in a solution made acid by the addition of niter cake or sulfur dioxide. Under these conditions, the original reaction is reversed with the production of a suitable sodium sulfite cooking liquor.

Bradley and McKeefe (23) have proposed several calcination methods in which the waste liquor is never fused; instead, it is dried and heated in a stream of air so that sulfur compounds are removed. The sodium salts (essentially carbonates) are then obtained by leaching the incinerated mass.

Smelting the waste liquor offers a logical method for the recovery of the inorganic constituents, because (a) the yield is high, even in practice, and (b) at the same time considerable quantities of heat are liberated, which substantially decreases the mill fuel and power costs. When monosulfite waste liquor is subjected to this process, a large quantity of sulfide is produced which forms thiosulfate during the subsequent sulfiting operation. Such a method has been patented by Bradley and McKeefe (24, 25) in its application to the Keeure process. By mixing waste liquors from an alkaline process with those of the neutral sulfite process (26), a residue is obtained after smelting which has a smaller ratio of sulfide, so that less thiosulfate is subsequently produced.

Because the normal constituents of the smelting process (sodium sulfide and carbonate) will yield a liquor after causticization which is normally used in the alkaline sulfate process, Bradley and McKeefe have obtained a series of patents based on a cross recovery between the two processes (27-29). Thus, the green liquor obtained from the monosulfite digestion is causticized and used in the sulfate process. It was proposed in these patents that the residual liquors from the sulfate recovery process might be sulfited and utilized in the monosulfite process.

In an effort to reduce the sulfide content resulting from fusion of these waste liquors, Drewsen (30) proposed the addition of 10-30 per cent of lime to the hot, concentrated liquor when the make-up soda is added in the form of niter cake. Fusion of this mixture produces calcium sulfide and predominantly sodium carbonate, which is leached from the fused mass. The calcium sulfide may then be suspended in water and converted, by the introduction of carbon dioxide, into calcium carbonate with the liberation of hydrogen sulfide. The escaping gas can be burned to form sulfur dioxide needed in the sulfiting operation, and the precipitated calcium carbonate may be calcined to produce the lime originally admixed with the waste liquor.

Haglund (31) used a roasting step following the usual fusion so that the final products are sulfate, sulfite, and carbonate with only traces of unreacted sulfide. The roasting was carried out in the neighborhood of 500° C., which is substantially above the decomposition temperature of sodium thiosulfate (240° C.). The resultant liquor was divided into two portions, one of which was subjected to treatment with sulfur dioxide after the addition of finely crushed calcium carbonate. The action of sulfur dioxide on the limestone resulted in the formation of calcium bisulfite with the liberation of carbon dioxide. This bisulfite, in turn, reacted with the sodium sulfate in the solution and formed sodium bisulfite and calcium sulfate. The remaining portion of the original liquor was then added to neutralize the bisulfite and remove any calcium which might have been present because of the solubility of the calcium sulfate.

The removal of sulfide by the use of water gas was proposed by Rawling (32). This was accomplished by introducing air and steam into the furnace at a suitable temperature so that it reacted with the carbon residue in the waste liquor. The sodium sulfide was thus converted to carbonate with the elimination of hydrogen sulfide, and the resultant ash was free of combined sulfur.

Billington, Chidester, and Curran (33) have demonstrated on a laboratory scale a very interesting process which can best be described in a series of steps:

1. Evaporation of the waste liquors.

2. Burning of these liquors in a spray-type furnace with the production of sodium sulfate, sulfide, sulfite, and carbonate. A large quantity of heat is also liberated in this operation.

3. The coarsely ground ash is mixed with sodium bicarbonate containing about 50 per cent moisture; the bicarbonate must be present in sufficient quantity to supply 2 moles of the bicarbonate for each mole of sulfide.

4. This mixture is heated to 200° C. at atmospheric pressure, so that sodium carbonate is formed and hydrogen sulfide is liberated. This gas is carried to suitable burners where it is converted to sulfur dioxide, which is subsequently required.

5. The incinerated ash of the preceding step is dissolved in water and carbon dioxide is passed into a portion of this solution, so that sufficient bicarbonate is formed for Step 3.

The solution of carbonate is then sulfited with the product from the burning of the hydrogen sulfide. This process is carried on

until the solution is saturated and contains only sodium bisulfite. During this operation, carbon dioxide is driven off and can be used to form the bicarbonate in Step 5. If sodium monosulfite is desired, the bisulfite must be neutralized with an aliquot portion of sodium carbonate.

Despite these several proposed methods for the utilization of waste liquors originating from the monosulfite process, Schacht (34) was early of the opinion that the process could find no industrial applications unless sodium salts became very cheap. This observation was based on the knowledge that sodium sulfide could be converted only to compounds which were of little or no value in the cooking process. However, the author stated that pulp produced by the neutral sulfite process was of exceptional quality and claimed priority for this method of cooking fibrous materials. He further suggested the possible use of sodium sulfite as a first step in the de Vains chlorination process, in place of the caustic soda commonly employed.

Clark (35) confirmed Schacht's observation on waste liquor recovery and stated that recovery in the full Keebra process is impractical because the reused cooking liquor causes a slowing of the pulping action and produces a black pulp. He stated, however, that one American mill, in continuous operation on a Semikeebra process, employed a considerable quantity of caustic soda in the cooking liquor in addition to the sulfite normally present. In this way, it was possible to sulfite only the make-up chemical in the form of soda ash and much difficulty with thiosulfate was avoided; 5 per cent thiosulfate was said to be the maximum allowable concentration. It should be further noted that the

waste liquor from any full Keebra cooks can be reused directly in the Semikeebra process, thereby recovering any unused active chemical.

Similar conclusions were reached by Drewsen (5), who admitted the excellence of the pulp but considered the process impractical because of the high chemical cost. He saw no advantage in the Semikeebra process and placed the maximum concentration of thiosulfate at 4 per cent. Further, this substance was characterized as a poison for the cooking liquor and, hence, should be avoided altogether.

The monosulfite process, therefore, is one which yields a very good pulp and has the added advantage that it can be successfully applied to many wood species. Its merits are particularly apparent when applied to resinous woods and hardwoods. The chief drawbacks to further commercial application are the lack of a good recovery system and the high chemical demand, which render the process too costly for general use. Many recovery systems have been proposed, some of which appear to have merit; however, the only one which has withstood the test of time is a cross-recovery process. In this operation the monosulfite liquor is prepared from the green liquor produced in a kraft recovery process, whereas the monosulfite green liquor, rich in sulfide, is used after causticization for the sulfate process.

## PRESENTATION OF THE PROBLEM

The purpose of this investigation was to examine the recovery system of the monosulfite process, which employs a fusion of the waste liquor followed by sulfiting of the products of the operation. Clark (36) has stated that, in commercial practice, the brightness of pulps obtained by the use of such regenerated cooking liquors is markedly reduced as compared with that attained by the use of fresh liquors. Consequently, the effect on pulp brightness of the constituents arising through this series of operations was a chief consideration. Further, because there is a rather complex group of chemical reactions involved, the determination of all constituents in the cooking liquors was of fundamental importance.

It was obvious that, before any studies of this nature could be undertaken, experimental fusions of waste liquors would be necessary. Consequently, the development of suitable experimental equipment and techniques for the recovery of the inorganic constituents of the cooking liquor became an important aspect of the investigation. This problem has been considered with a view of adhering as nearly as possible to the general commercial procedures, so that any apparatus constructed may be used as a pattern in similar work on other studies of recovery systems in general.

The problem is thus resolved into two parts: first, the development of a laboratory recovery unit and, second, studies of the recovery system in the monosulfite process. The aims of the second part are (a) the determination of the chemical substances present in the liquor, and (b) the study of the effect of these materials on the brightness of neutral sulfite pulp.

## APPARATUS

### SMELTING CRUCIBLE

#### Material of Construction

The conditions of the smelting operation are such that the crucible must be resistant to molten alkali and sulfides in a reducing atmosphere at temperatures in the neighborhood of 1000° C. Most of the com on nonmetallic refactories (for examole, alundum, sillimanite, fused silica, magnesia, zirconium oxide, and others) can ot be used because of their solubility in alkelies. On the other hand, although the temperature requirement is not inconsistent with the use of many metels, of those which are resistant to alkali there appears to be none which can ne used with sulfides. This is true of platinum, which is considered one of the most inert of materials avail·ble for laboratory apparatus.

Soapstone is a very com on refractory in industrial recovery instatlations. It should be remembered that such units, because of their size and the exothermic nature of the reaction, are internally heated. On the laboratory scale, however, the reaction would supply insufficient heat to attain the desired temperature, because the ratio between the surface and capacity of a furnace is not constant with furnace size, but increases with decreasing furnace volume. As a result, high temperatures can be obtained only by external means, and it is obvious that, in a laboratory unit, the face of the crucible contacting the smelt will be the coldest portion of the refractory, whereas the opposite

is true with industrial equipment. Experience has shown that, although soapstone exhibits admirable resistance in the industrial recovery unit, it crumbles easily and is unsatisfactory when externally heated as is necessary in this particular application.

Since this study deals with a reducing atmosphere, graphite comes into consideration. Further, because the smelting operation has as its chief purpose the removal of organic materials by conversion to carbon and ultimately its gaseous oxides, it is obvious that graphite, which is nearly pure carbon, can contribute few impurities to the fused material, even if there is considerable erosion during the operation. Preliminary experiments with a crucible made from electrode graphite (National Carbon Company) confirmed these suggestions and produced very satisfactory melts. Surprisingly enough, very little surface erosion took place. However, repeated use of the same graphite crucible revealed the chief objection to its use—the fact that, although the walls showed little surface erosion, they rapidly became porous and were permeated by a considerable quantity of the fused salts. In general, such a crucible was worthless after two fusions. Probably explanations for this behavior are: (a) the graphite undergoes a change in grain size on strong heating, and (b) the small percentage of binder present in the graphite is dissolved by the fused alkali, which then penetrates the crucible wall.

Several materials available in a plastic form were used as linings on a graphite base. Chromite ore, a naturally occurring mineral, showed the greatest promise, because it was unaffected by

the fused salts. However, the nature of the coating was such that it proved quite ineffective in preventing the penetration of the molten material into the wall. This material is not available in crucible form, and attempts to form an impervious crucible in a mold were not successful.

The use of a more impervious form of graphite, sold by the U. S. Graphite Company under the trade name of "Graphitar," was investigated. This product finds frequent use as gaskets, allowing confinement of gases, particularly nitrogen and freon (dichlorodifluoromethane), under high pressures. Several Graphitar crucibles were made and found to have a useful life roughly three times that of the ordinary graphite crucibles. Eventually, the walls were penetrated as with the common variety, but their prolonged resistance supports the idea that the cause of the porosity is the removal of the binding material. (Graphitar has much less binder and is produced from carbonaceous materials as far as is practicable.)

On the basis of these tests, graphite or Graphitar was employed as the material of construction. It should be noted that these materials, especially graphite, possess the very important property of ease of machining. Thus, they can be readily threaded, tapped, or tapered, and joints can be ground to a close fit. All machining of the crucibles constructed was done in a lathe.

Crucible Design

Because it was an objective of this work to adhere as closely

as possible to industrial practice, it became necessary to devise a method of introducing the molten salts directly into water at the conclusion of the smelting operation, this being the procedure in common use. There were two ways in which this could be accomplished: (a) by actually tilting the crucible or possibly the entire furnace while the crucible was still in place, and (b) by releasing the smelt through the removal of a plug or cock so that the fused material would be free to fall into the dissolving tank.

The latter alternative was chosen after the size and weight of the crucible and furnace had been taken into consideration. It was decided to use a centrally located plug which would fit into a tapered tap hole in the bottom of the crucible. This plug passed through the crucible and outside the furnace, extending several inches above the cover so that it could be operated easily without removing either the crucible or furnace cover, which was constructed with the necessary hole. Because the plug passed through the smelting area, it was constructed from a graphite rod; a close fit at the tap hole was insured by grinding the two members in place.

Although this apparatus was used in several experiments, it was far from satisfactory. The chief difficulty was the fact that any jar displaced the plug sufficiently to allow seepage of the smelted material. Also, when the plug was lifted at the conclusion of the operation, the egress of the fused substance occurred with such speed that an extremely explosive action resulted from its contact with the water. These difficulties were eliminated by threading the upper portion

of the crucible and constructing a threaded cover of suitable size, which could then be fixed securely in place. The plug was also threaded and screwed into a threaded hole in the center of the cover. Upon tightening, the plug was held firmly in place at the tapered tap hole and did not move despite moderate jarring and bumping. This arrangement had an added advantage in that, when releasing the smelt, the plug could be screwed up slowly and the rapidity of the introduction of the smelt into the dissolving tank was controlled in this manner. With this set-up, it was necessary to provide a hole in the cover to allow charging the crucible with ground black liquor solids. A 3/4-inch tapped hole proved adequate, and a graphite plug having a smaller hole for the escape of gases was screwed in place after filling.

Thermocouple

A temperature-measuring device was needed within the smelting area. Consequently, a chromel-alumel couple was placed within the rod serving as a plug. This proved an admirable location, because it was approximately in the volumetric center of the crucible and gave a very nearly true indication of the existing temperature within the crucible, as will be shown in the next paragraphs. A Weston microammeter (Model 440) was used as the temperature-indicating device, and a 600-ohm, 1-watt fixed resistance was placed in series with the couple so that the temperature range would give readings within the scope of the instrument.

Thermocouple Calibration

The manufacture furnishes tables showing the potential

developed by the chromel-alumel couple at various temperatures, which can be translated into amperes by a simple calculation of Ohm's law if the total circuit resistance is known. This resistance was determined by the use of an impedance bridge, and the readings were plotted against temperature as shown in Figure 1.

With the thermocouple in place in the plug rod, the thermocouple was also calibrated by using an optical pyrometer as a standard. This instrument was focused on the 3/4-inch loading hole, which was small in comparison with the total volume and consequently served as an approximation to a perfect black body. In order to facilitate reading of the optical pyrometer, the direction of viewing was changed from the vertical to the horizontal by the use of a suitably placed front-faced mirror. The reflectance of this mirror was determined by the use of the General Electric recording spectrophotometer and taken into consideration in subsequent calculations.

The results of this calibration are in excellent agreement with the calculated data shown in Figure 1. It may be concluded that the thermocouple gives the true furnace temperature, within suitably close limits.

Thermocouple Protection Tube

In the early set-up, the thermocouple was placed directly into a hole drilled in the rod. However, it was soon discovered that the severe reducing conditions existing within the rod rapidly attacked the wire, which became brittle and broke under the slightest stress.

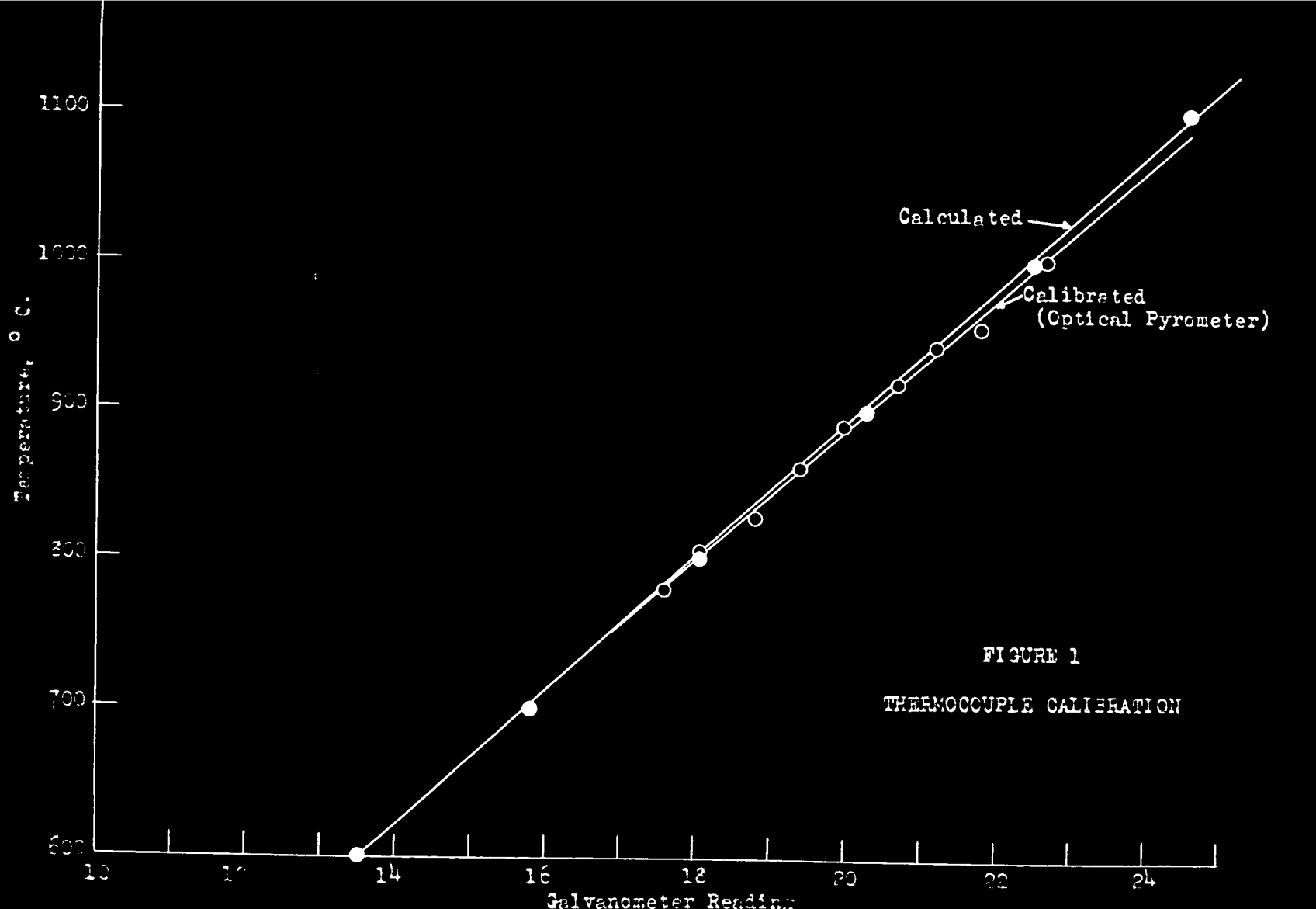



FIGURE 1

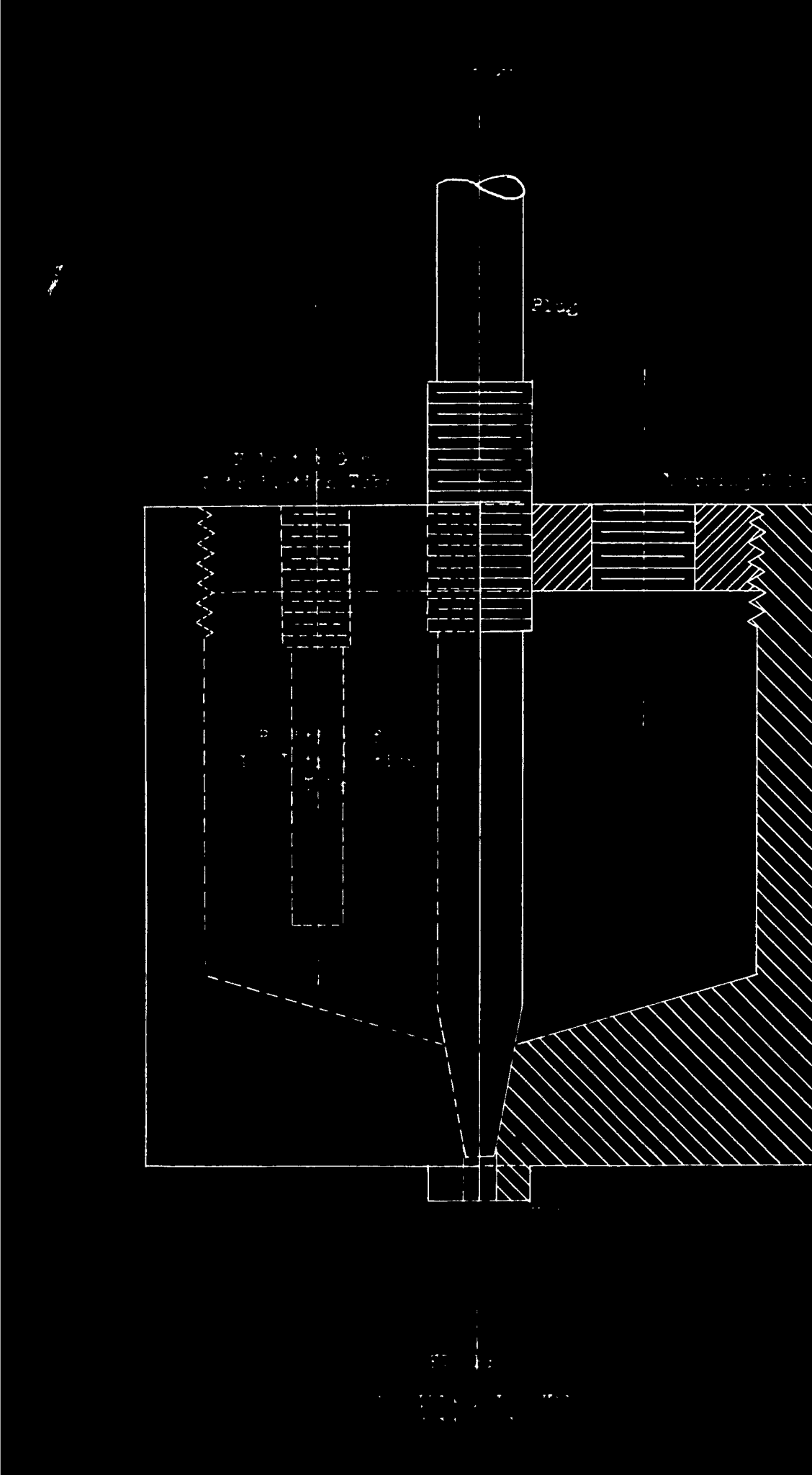
THERMOCOUPLE CALIBRATION

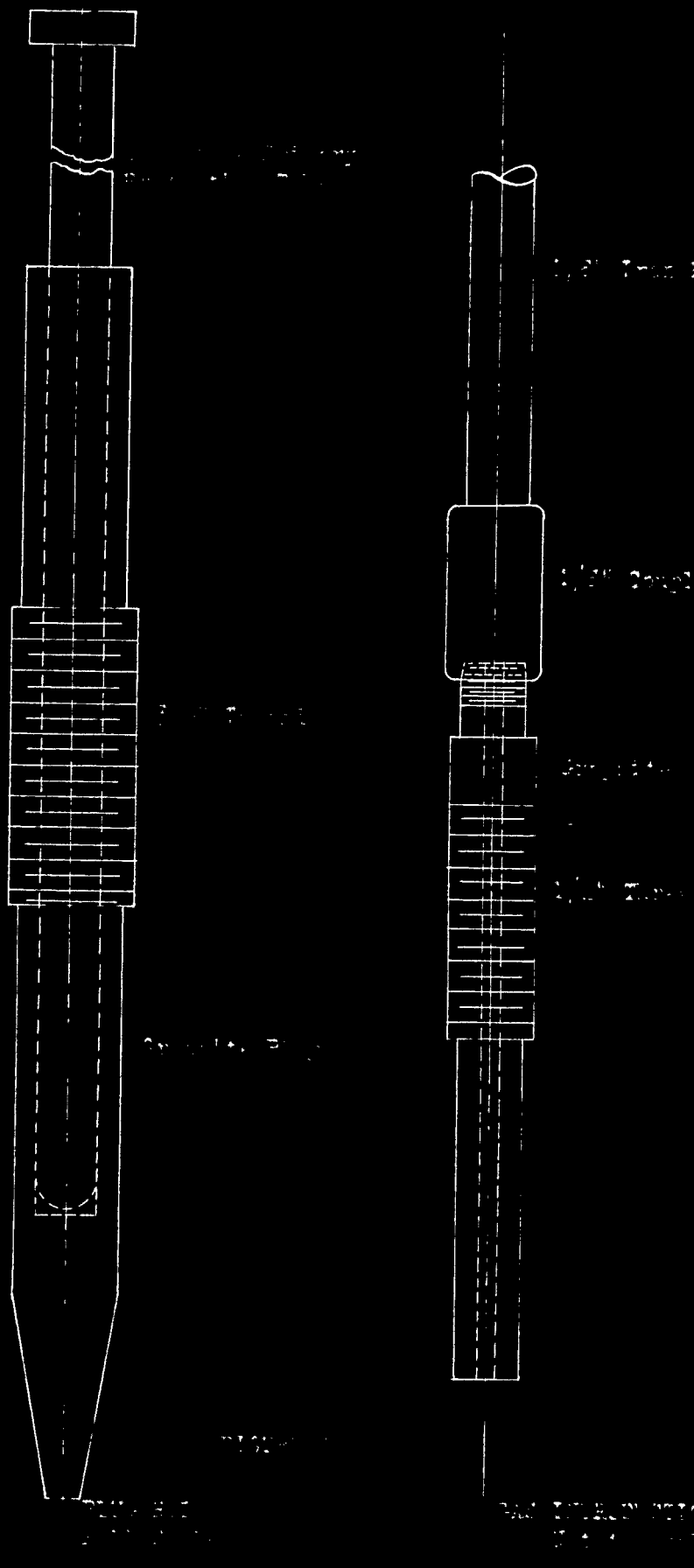
This undesirable condition was eliminated by the use of a Supertite primary protection tube of the type commonly employed in industrial pyrometry. Care must be taken to burn off the organic substances in the wire insulation before placing the thermocouple within the tube. If this precaution is not taken, the decomposition of these materials produces strongly reducing conditions within the tube and the attack on the thermocouple wires is not eliminated.

GAS INTRODUCTION TUBE

Entry for the oxidizing substance required in the combustion of organic material present in the waste liquor was provided by a gas introduction tube. This tube was made from a graphite rod through which a small hole had been drilled. At a point several inches from the lower end, the tube was threaded with a 1/2-inch standard thread so that it could be fitted into a tapped hole in the graphite cover, allowing the tube to extend several inches into the crucible as shown in Figure 2. At the upper end, which extended outside the furnace, the rod was fitted with a 1/8-inch pipe thread and was coupled at this point to a piece of 1/8-inch iron pipe. This arrangement so extended the tube above the furnace that it was possible to connect it with a compressed gas tank by means of rubber tubing without the hazard of burning the rubber. A suitable hole in the furnace cover was required.

Detailed and assembled drawings of the crucible and its component parts are given in Figures 2 and 3.





FURNACE

The furnace used for the experimental smelts was a common crucible type manufactured by Hoskins (FD-104) and was heated by means of a chromel heating unit. Several changes in the construction were necessary to permit the dumping of the fused salts.

EXIT TUBE

A hole 1 inch in diameter was bored through the sandstone insulation and transite bottom cover of the furnace and a sillimanite tube was fixed in place with alundum cement. Because the tap hole in the bottom of the crucible was only 1/4 inch in diameter, the major portion of the smelt did not contact the tube and the chemical attack was slight.

In order to eliminate any tendency for the smelt to freeze in the exit tube, it was wound with an auxiliary heating coil of chromel wire and provided with the necessary electrical circuit, including rheostats and an ammeter. The temperature gradient throughout the length of the tube was made as nearly constant as possible by spreading the wires along the tube; thus, at the bottom the wires were closely wound and gradually spread out so that, at the upper end, the auxiliary heater contributed no heat to the tube. It must be remembered that the upper portion was heated by the furnace itself, whereas the lower portion would normally be much cooler. Visual observation showed the tube to have a uniform cherry-red color when in operation, and no difficulty was experienced with the smelt freezing after the installation of this

heater. However, at the completion of the smelting operation, a small quantity of frozen salt remained at the lower end of the exit tube. This was removed, after the furnace had cooled, by a small stream of water directed down the tube and conducted to the drain by a powder funnel fastened to a rubber tube.

HEATING UNIT LIFE

A very troublesome difficulty was encountered in the very short life of the furnace heating element. The cause was undoubtedly the reducing atmosphere which existed as a result of the gaseous products of combustion and which inevitably found their way into the heating area. To alleviate this condition, ducts were constructed leading from the bottom of the furnace to the heating element. By this means gas could be passed up around the element and out of the furnace around the sides of the upper cover. An inert gas (nitrogen) was employed at first, but it was later found that better results were obtained by the use of air which could be passed through at a fairly rapid rate and kept the unit surrounded by a definitely oxidizing medium. The construction details are shown in Figure 4.

INERT ATMOSPHERE FOR CRUCIBLE

When the furnace was heated, a natural draft was created up through the bottom tube and out through the upper portion of the furnace. This flow of air caused a serious erosion of the crucible, especially in the area around the tap hole. This condition was greatly improved by the construction of a graphite plug which fit into the exit tube and




FIGURE 4

FURNACE DETAILS

carried a small sillimanite tube through which nitrogen was passed. As a result, the crucible was in a nitrogen atmosphere at all times and was unaffected to any marked degree by combustion of the outer wall.

In order to provide space for these various connections under the furnace and to permit the placing of a dissolving tank below the exit tube, the entire furnace was placed on a transite table with four 10-inch legs constructed from 1 1/4-inch standard pipe. This table had a large circular hole in the center which permitted ready access to the electrical leads and the exit tube.

LIQUOR DISSOLVING TANK

When the molten smelt is dropped into water, the action is rather violent and a considerable quantity of water is thrown from the containing vessel. In order to reduce this action as much as possible, a tank 6.5 inches in diameter and 5-5/8 inches high was constructed from thin sheet metal, and a cover was provided which carried a centrally placed metal cylinder extending vertically upward 3 inches above the cover. The cover is further provided with three 3/4-inch holes which are baffled. The tank is thus a modified form of a muffler, in that it fits closely to the furnace exit tube and the area increases greatly at the liquor level. The escape of liquor is prevented by the baffles on the relief holes. The details of this tank are shown in Figure 5.

A small stainless-steel stirrer was placed in the tank in an effort to insure uniformity of the liquor. Temperature uniformity was especially desirable because, with proper mixing, the temperature of

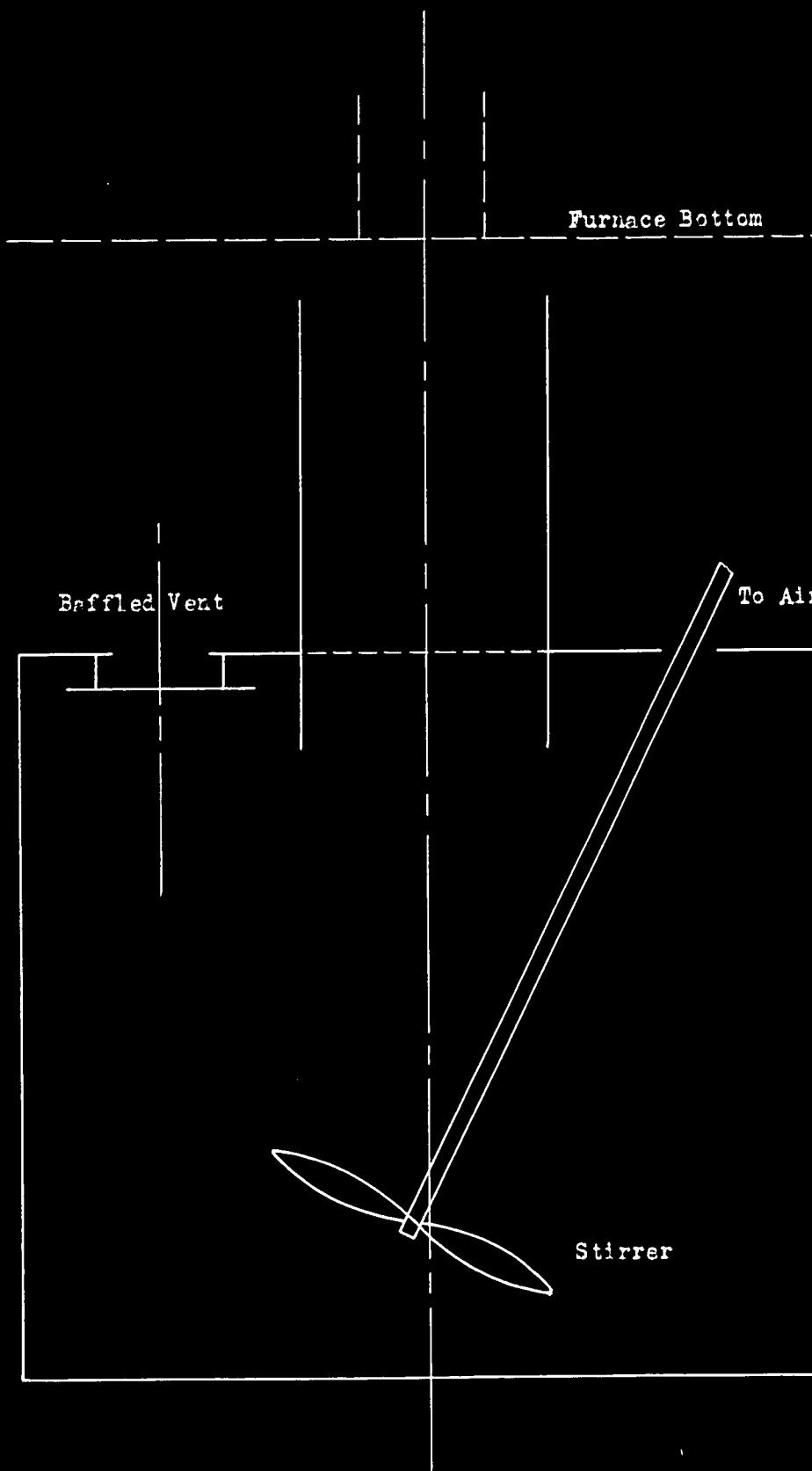



FIGURE 5

SMELT DISSOLVING TANK
Scale 3/8" = 1"

the solution did not reach the boiling point; however, without the stirring device there was an opportunity for local overheating and boiling. The stirrer was powered by a small air motor which was chosen primarily for its size. The entire dissolving tank was painted with a white chlororubber paint which withstood chemical attack admirably. In operation, the tank was blocked into position by four iron rods which made contact with the tank every 90 degrees and effectively held it in place. These rods were supported by clamp holders placed on the legs of the furnace.

## EXPERIMENTAL METHODS

### LIQUOR PREPARATION

In the preparation of neutral sulfite cooking liquor, the obvious objective is to achieve maximum conversion of chemical to the monosulfite, representing a condition characterized by a proper pH and a minimum quantity of bicarbonate. In case the starting material is pure sodium carbonate, one equivalent of bicarbonate will be formed for each equivalent of monosulfite, if the reaction is carried out by bubbling sulfur dioxide through the solution until the desired pH (about 8.0-8.5) is attained. This is expressed by the equation:

$$2\ Na_2CO_3 + SO_2 + H_2O \longrightarrow Na_2SO_3 + 2\ NaHCO_3.$$

In practice, this step is generally carried out by trickling the solution through a packed tower in which sulfur dioxide is ascending. This results in a saturation of the solution with the gas, and carbon dioxide is driven off:

$$Na_2CO_3 + 2\ SO_2 + H_2O \longrightarrow 2\ NaHSO_3 + CO_2.$$

The liquor has a pH of approximately 4 when it leaves the tower and is neutralized when it runs back into the original solution. If this return is stopped at a pH of 8.0 to 8.5, the final reaction may be represented:

$$NaHSO_3 + Na_2CO_3 \longrightarrow Na_2SO_3 + NaHCO_3.$$

Theoretically, the net conversion effected by such a procedure represents the formation of two equivalents of monosulfite and one of bicarbonate, as opposed to the 1:1 relationship achieved by the direct sulfiting of the sodium carbonate to the same pH.

If the liquor produced in the tower is not returned to the original solution but is collected in a separate container and neutralized by running the original liquor into the new acid solution, the resultant liquor would contain only monosulfite:

$$2\ NaHSO_3 + Na_2CO_3 \longrightarrow 2\ Na_2SO_3 + CO_2 + H_2O.$$

However, a certain alkalinity is desired in the cooking liquor so that an excess of the carbonate would always be added. Because of the carbon dioxide present in the solution, this excess would be converted to bicarbonate in the cooking liquor.

Although a tower was not used in the laboratory, the same steps were followed by converting an aliquot of the liquor to a pH of 4 and subsequently neutralizing it with the remaining solution. Finally, an excess of the original solution was added to adjust the pH to the desired value of 8.0 or 8.3. This same procedure was followed in dealing with the recovered liquors.

EXPERIMENTAL COOKING

Three small stainless-steel autoclaves having a capacity of 6 liters were used for the cooks. These digesters were heated by means of individual wax baths which insured uniform heating throughout. The autoclaves were fitted with the necessary relief lines, pressure gages, and thermometer wells; temperature was used as the cooking control because of the difficulty of relieving all the digesters to exactly the same point; therefore, the pressures varied slightly from time to time.

Cooking conditions were determined by several experiments and,

although they are not suggested as the optimum, the base pulps were very satisfactory. The conditions for the base cook were:

| | |
|---|---|
| Chemical addition | 30% $Na_2SO_3$ as $Na_2O$ |
| Temperature at maximum | 180° C. |
| Time to maximum temperature | 1.5 hours |
| Time at maximum temperature | 6 hours |
| Wood charged | 600 g. (oven dry) |
| Water ratio | 6:1 |

Some of the conditions, particularly the time at maximum temperature and the chemical addition, were varied in the experimental work, but the others were unchanged.

At the completion of the cook, the pressure was relieved and the waste liquor collected. The cooked chips were then washed as completely as was feasible, still keeping the water volume low. The original waste liquor plus the first and second wash liquors were collected for subsequent treatment.

Because it was impossible to blow the cook and thus break up the cooked chips, the pulp was obtained in chip form after cooking. These chips, however, were soft and readily broke up in the British disintegrator; 600 revolutions of the counter were found to give good results, and this treatment was arbitrarily fixed as standard. As a consequence, the screened yield has little quantitative value and only the unscreened values are reported. After disintegration, the pulp was washed, screened, and rewashed. These operations were followed by the formation of brightness sheets, determination of yield, etc.

LIQUOR CONCENTRATION

The waste liquor, plus the first and second washings, was concentrated to about 50 per cent solids in a vacuum distillation apparatus. Vacuum concentration was employed because of its convenience and not because of any effect which heat might have on the organic products present in the waste liquor. By this system, however, bumping—always a hazard at atmospheric pressure—and excessive foaming were eliminated.

After this preliminary concentration, the waste liquor was evaporated to complete dryness in an oven at 125° C. The drying operation required about 24 hours, and the product was a hard vitreous mass which, being brittle, could be pulverized easily with a mortar and pestle.

SMELTING

With the cover and plug screwed firmly in place as previously described, the dried black liquor solids were charged into the crucible. The temperature was then raised by means of the heating unit, the increase being followed by readings taken with the thermocouple. During this preliminary heating there was little or no chemical reaction, although the material within the crucible became rubbery and expanded somewhat in volume.

It was decided to use carbon dioxide as the oxidizing material, in that it reacts with carbon forming the monoxide:

$$CO_2 + C \longrightarrow 2\ CO.$$

This compound was chosen for two reasons: (a) the crucible erosion resulting from oxidation of the graphite would be somewhat diminished, and (b) it would conform most nearly to the conditions actually present in the industrial recovery process. Although air is forced into the commercial unit, the oxidizing zone where the product of combustion is carbon dioxide is very small, the remainder being a reducing zone in which carbon monoxide is the chief compound present. Consequently, the experimental method is a good approximation to industrial practice.

Carbon and carbon dioxide form an equilibrium mixture with the product of their reaction, carbon monoxide. The relative proportion of carbon monoxide present is greatly dependent upon the existing temperature (37), as shown by the following table:

| Temperature ° C. | Percentage by Volume CO | $CO_2$ |
|---|---|---|
| 450 | 2 | 98 |
| 750 | 76 | 24 |
| 850 | 93.8 | 6.2 |
| 950 | 98.7 | 1.3 |
| 1050 | 99.6 | 0.4 |

It is evident that above 800° C. the reaction is carried very nearly to completion; it should also be noted that there is a favorable balance at about 700° C.

As a result of these facts, carbon dioxide was passed into the crucible very slowly during the preliminary heating—i.e., until 700° C. had been attained. This was done to prevent the gas introduction tube from being plugged. When the threshold temperature was

reached, however, the gas rate was increased to approximately 12 cubic feet per hour and the total volume of gas introduced was recorded by means of a Sargent wet test meter through which it passed. Rough calculations of the volume required were made by considering the charged waste liquor solids as pure carbon and determining the stoichiometric quantity of carbon dioxide required for its combustion. This method insured an excess of the oxidizing material since the inorganic constituents would not react. The maximum temperature was approximately 1000° C. A rough check on this operation was obtained by successive smelts on the same waste liquor solids; the results were in excellent agreement from the standpoint of the ratio of the constituents.

DISSOLVING THE SMELT

Shortly before the conclusion of the smelting operation, the plug was removed from the bottom of the exit tube and the auxiliary heater was connected in its electrical circuit. The necessary water was poured into a dissolving tank, which was then pushed in place and fixed by means of the four rods. The air stirrer was started and the apparatus was ready for dropping the smelt. This was accomplished by unscrewing the plug slowly while the fused material ran from the crucible. When it was so desired, one smelt could be dropped into the green liquor produced by a previous experiment and in this way the salt concentration could be increased.

ANALYTICAL METHODS

Liquor Analysis

The following analytical determinations were carried out on

the white and green liquors:

Total Sodium (Institute Method 104). The sodium was precipitated as sodium uranyl zinc acetate and determined gravimetrically.

Total Sulfur (Institute Method 107). All sulfur compounds were converted to sulfate through oxidation with 30 per cent hydrogen peroxide. The sulfate ion was then precipitated from a slightly acid solution with barium chloride and weighed, after ignition, as barium sulfate.

Sulfate (Institute Method 107). Interfering sulfur compounds were removed by treatment with acid and subsequent filtration. The sulfate was precipitated with barium chloride and determined gravimetrically.

Reducing Agents—Sulfide, Sulfite, and Thiosulfate (Institute Method 107). These compounds were determined by a series of iodometric titrations, in which one component was removed at each step. The individual components were then determined by difference. Use was made of the aldehyde-bisulfite addition product as suggested by Moltzau (38). In this manner the sulfite can be prevented from reacting in a solution rendered acid with acetic acid, which converts the sulfite to bisulfite and does not liberate sulfur dioxide.

Sulfide. The total reducing agents were determined by running the liquor aliquot into a known quantity of acidified standard iodine solution and back-titrating. The sulfide is the difference between this titration and that for thiosulfate and sulfite.

Sulfite. Any sulfide was removed by precipitation with a fresh zinc carbonate suspension. In dealing with white liquors which have a high sulfite content, care must be taken that no zinc ions are present. If zinc ion is present in the solution, sparingly soluble zinc sulfite will be precipitated as its solubility product will be exceeded. This compound has a normal solubility of 0.16 parts per 100 parts of water. It is possible to eliminate any precipitation by diluting the liquor aliquot sufficiently, although in that case the titration volume of standard solution is correspondingly reduced, resulting in decreased precision of the determination. It is felt that a better method of accomplishing this result is to provide an excess of carbonate in the zinc carbonate suspension. Should this condition remain uncorrected, however, the precipitation of zinc sulfite results in sulfide determinations which are too high, whereas the sulfite is erroneously low.

Having removed sulfide from the solution by precipitation, the thiosulfate and sulfite were determined by running an aliquot into an excess of acidified iodine solution. The excess was then back-titrated. The equivalents of sulfite and thiosulfate subtracted from the total reducing constituents gave the sulfide; the thiosulfate (as determined below) was subtracted from this determination for the sulfite.

Thiosulfate. An aliquot of the sulfide-free liquor was run into a formaldehyde solution made acid with acetic acid. The sulfite was combined as the bisulfite-aldehyde addition product, whereas the thiosulfate was free to react with iodine. An excess of iodine was run

into the solution and immediately back-titrated. The thiosulfate thus determined was subtracted from the sum of the sulfite and thiosulfate for the determination of sulfite. The excess of iodine should never exceed one milli-equivalent for accurate results.

Carbonate or Bicarbonate (Institute Method 107). Bicarbonate in the liquor was calculated from the determination of the total alkali by subtracting the correct sulfide and sulfite equivalents. The total alkali determination was carried out by titration of the liquor aliquot with standard acid to the methyl orange end point in the presence of an aldehyde, so that any sulfite present was titrated quantitatively to the bisulfite. In this case Moltzau (38) showed that furfural must be used; otherwise, a certain portion of the thiosulfate will be titrated. The method is directly applicable to green liquors, and the carbonate is calculated by subtracting the equivalents of sulfide and half the equivalents of sulfite (the sulfite is only carried to the bisulfite) from the total alkali.

However, this method cannot be employed with all white liquors. Some liquors were prepared having a pH of 8, which is slightly below the value for sodium sulfite, and it must be assumed that a certain portion is present as bisulfite and cannot be determined. Consequently, the value to be subtracted from the total alkali is not known and the bicarbonate cannot be calculated. This problem was solved through the expedient of using liquors of a pH of 8.3, so that, essentially, the normal sulfite, bicarbonate, and hydrosulfide are present in the liquor. The total alkali then evaluates all of these constituents; the bicarbonate

can be determined by subtracting one-half the equivalents of sulfite (sulfite carried to bisulfite) and one-half the equivalents of sulfide (present as hydrosulfide at a pH 8.3) from this value.

Pulp Analysis

The following determinations were carried out on pulp samples:

Lignin (Institute Method 428). The Klason lignin determination was used employing 72 per cent sulfuric acid, followed by a hydrolysis at 3 per cent. In some cases 1-gram samples were employed instead of the standard 2-gram standard samples to facilitate filtering.

Permanganate Number (Institute Method 410). Forty ml. of the 0.1 N permanganate solution were used.

Iron (Institute Method 429). The pulp was ashed, the ash taken up in 10 per cent hydrochloric acid, and the iron determined in a calibrated photoelectric photometer by means of the intensity of color produced by the formation of ferric thiocyanate.

Total Sulfur. The modified Klingstedt method of Larson (39) was used. The pulp was refluxed with fuming nitric acid, which destroys the organic material and converts all sulfur compounds to sulfate. After removing all traces of nitric acid by the repeated addition of hydrochloric acid and evaporation to dryness, the sulfate was determined gravimetrically by precipitation as barium sulfate.

## PRESENTATION OF DATA

### COMPOSITION OF GREEN LIQUORS

During the fusion of the monosulfite waste liquor solids, the sulfur compounds are subjected to a reduction at high temperatures. Sulfur occurs in these solids as unconsumed sodium sulfite and probably in combination with the solubilized lignin (possibly as a sulfonic acid salt). It is logical to assume that in fusion reduction, sulfide will be the chief product because it is known that sodium sulfate is readily converted into the sulfide by elementary carbon.

$$Na_2SO_4 + 4\ C \longrightarrow Na_2S + 4\ CO.$$

In order to determine the exact composition of the liquor resulting from this operation, a series of sulfur balances were made. In each case the individual constituents were determined iodometrically, whereas the total sulfur was obtained through oxidation and precipitation as the sulfate. These balances are given in Table I.

TABLE I

CONSTITUENTS OF THE GREEN LIQUOR PRODUCED BY THE SMELTING OPERATION

Grams per Liter as Sulfur

| Waste Liquor from Cook | 1 | 2 | 101 |
|---|---|---|---|
| Sodium sulfide | 7.6 | 14.8 | 26.3 |
| Sodium sulfite | 0.1 | 0.1 | - |
| Sodium thiosulfate | 0.2 | 1.2 | 3.1 |
| Sodium sulfate | 0.1 | 0.9 | 0.9 |
| Total sulfur (from individual analyses) | 8.0 | 17.0 | 30.3 |
| Total sulfur (found by direct determination) | 8.2 | 17.7 | 31.1 |

These balances agreed to within about 2.5 to 3 per cent. This might be considered the limit of experimental error, because the precipitation was carried out in the presence of other compounds (especially the carbonate), and the phenomenon of coprecipitation was to be expected.

The sodium balance was subject to greater intrinsic error, because the determination of the carbonate was dependent upon several other determinations and the errors were cumulative with a resulting decrease in precision. The analysis of the liquor from Cook 101 is given in Table II.

TABLE II

SODIUM AND SULFUR BALANCES ON GREEN LIQUOR

Waste Liquor from Cook 101

| | Sulfur g./l. | Sodium as $Na_2O$ g./l. |
|---|---|---|
| Sodium sulfide | 26.3 | 50.9 |
| Sodium thiosulfate | 3.1 | 3.0 |
| Sodium sulfate | 0.9 | 1.7 |
| Sodium carbonate | - | 53.9 |
| Total (from individual analyses) | 30.3 | 109.5 |
| Total (found by direct determination) | 31.1 | 115.5 |

The error in this case (about 5 per cent) was somewhat higher than that obtained with the sulfur balance and attributable to decreased precision in the carbonate determination.

On the basis of these results, it may be concluded that all the sulfur was accounted for in the sulfide, sulfite, thiosulfate, and sulfate constituents. Sulfide and carbonate were the chief products of this operation, although the other constituents existed in varying and much smaller quantities. Causes of these variations were probably differences in the smelting procedure and in the composition of the black liquor solids. A check on the reproducibility of the operation was obtained by duplicate fusions on the same batch of waste liquor, using identical smelting schedules. These results are given in Table III and are expressed as the percentage of total sulfur for a better comparison, because the quantity of waste solids varied somewhat.

TABLE III

ANALYSIS OF GREEN LIQUORS OBTAINED BY DUPLICATE FUSIONS ON THE WASTE LIQUOR OF COOK 1

| | A % | B % |
|---|---|---|
| Sodium sulfide | 95.6 | 96.0 |
| Sodium sulfite | 1.1 | 0.9 |
| Sodium thiosulfate | 2.0 | 1.9 |
| Sodium sulfate | 1.3 | 1.3 |

SULFITING REACTIONS

The reaction between sulfur dioxide and solutions rich in sulfide is known to lead to a series of complex reactions (40). In this discussion the green liquors, which have been shown to contain small amounts of other constituents, will be regarded as mixtures of only sulfide and carbonate. Although there is some error inherent in

such an assumption, it is felt that any conclusions made on this basis will have fundamental value in consideration of the theoretical sulfiting operation.

It will be recalled that the method for liquor preparation outlined above requires the sulfiting of the liquor aliquot to a pH of 4 and subsequent neutralization, so that the by-product (bicarbonate) will be kept at a minimum. During the initial passage of sulfur dioxide into the solution, sulfur is liberated and thiosulfate is formed as a result of the reaction with sulfide.

$$2\ Na_2S + 3\ SO_2 \longrightarrow 2\ Na_2S_2O_3 + S.$$

The sulfur at first appears in a colloidal state as a white or yellowish turbidity. Because the carbonate is also present in the solution, sodium sulfite is formed simultaneously, which will dissolve the liberated sulfur and produce more thiosulfate. The over-all reaction may be considered as taking place between sodium sulfide and bisulfite:

$$6\ NaHSO_3 + 2\ Na_2S \longrightarrow 2\ Na_2SO_3 + Na_2S_2O_3.$$

When all the sulfide has been converted in this manner, the solution again becomes crystal clear; this condition corresponds very closely to the neutral point.

There is little or no reaction between the thiosulfate and sulfur dioxide while the solution is alkaline. However, as the solution becomes acid by the continued introduction of sulfur dioxide, the reaction between these compounds results in the formation of polythionic acid and its salts. An intermediate addition compound between the thiosulfate ion and sulfur dioxide has been suggested, which is said to be yellow in

color. This compound has been observed, the yellow solution of which has been found to be quite stable, remaining crystal clear with no precipitation of sulfur for several days. The formation of this complex prevents the decomposition of the thiosulfate ion into sulfur, according to the reaction:

$$S_2O_3^{=} \longrightarrow S + SO_3^{=},$$

and instead favors the conversion into polythionates,

$$2\ S_2O_3^{=} \longrightarrow S^{=} + S_3O_6^{=},$$

in as much as the sulfide ion is removed from the solution by reaction with the excess of sulfur dioxide. In this way the intermediate thiosulfate is held constant, whereas trithionate is formed by the sulfur dioxide.

There exists the possibility of formation of the higher thionates (e.g., tetrathionate and pentathionate); however, these would revert to trithionate because of their reaction with sodium sulfite. Consequently, the solution at a pH of 4 contains sodium bisulfite, sodium trithionate, and a certain amount of thiosulfate in equilibrium with the latter product.

When this solution is neutralized with the liquor aliquot, which contains sulfide and carbonate, the trithionate is broken down. This is accomplished by the sodium sulfide which reacts as follows:

$$Na_2S_3O_6 + Na_2S \longrightarrow 2\ Na_2S_2O_3.$$

If insufficient sulfide were added, this would not be the case. However, in the experimental work it has been found that an excess of sulfide is always present if equal aliquot portions of the same starting liquor are used.

COMPOSITION OF WHITE LIQUORS

The liquors resulting from the sulfiting operation were analyzed in much the same manner as the green liquors. The sodium and sulfur balances on two liquors are given in Table IV.

TABLE IV

SODIUM AND SULFUR BALANCES ON WHITE LIQUOR

| | S g./l. | $Na_2O$ g./l. |
|---|---|---|
| **Liquor - Cook 101** | | |
| Sodium sulfite | 27.4 | 53.1 |
| Sodium thiosulfate | 31.6 | 30.6 |
| Sodium sulfide | 1.1 | 2.0 |
| Sodium sulfate | 1.1 | 2.1 |
| Sodium carbonate | - | 11.1 |
| Total (from individual analyses) | 61.2 | 98.9 |
| Total (found by direct determination) | 62.0 | 105.3 |
| **Liquor - Cook 102** | | |
| Sodium sulfite | 42.3 | 82.0 |
| Sodium thiosulfate | 48.5 | 47.0 |
| Sodium sulfide | 2.2 | 4.3 |
| Sodium sulfate | 2.7 | 5.2 |
| Sodium carbonate | - | 10.7 |
| Total (from individual analyses) | 95.7 | 149.2 |
| Total (found by direct determination) | 97.9 | 156.0 |

In these examples, the discrepancy between the sulfur

balances is also about 2.5 per cent, whereas that of the sodium balances is roughly 5 per cent. This fact supports the theory that this is caused by differences inherent in the analytical methods.

On the basis of these determinations, it was concluded that the constituents of the white liquor had been accounted for by the analytical methods. Although polythionates escape detection by iodometric methods (41), it is known that any such compounds would be oxidized to the sulfate by 30 per cent hydrogen peroxide and detected in that way. However, the agreement between the sums of the individual tests and total sulfur and sodium by direct determination preclude the presence of substantial quantities of these substances. Therefore, it can be stated that polythionates are not present in any marked quantity.

EFFECT OF LIQUOR COMPOSITION ON PULP QUALITY

A preliminary series of cooks were made in order to ascertain the effect on pulp brightness of changes in the composition of the cooking liquor as a result of recovery operations. The liquor was obtained by smelting the waste liquor solids and analyzing the resultant green liquor; a synthetic green liquor of similar composition was then prepared from pure chemicals and, after sulfiting, was used as a cooking liquor. The total reducing power of the liquor was held constant throughout this series. Although it was evident that thiosulfate was present, the pulping qualities of this compound has not been sufficiently investigated, and hence no basis for comparable cooking conditions exists. Aronovsky (42) had stated that thiosulfate is a pulping agent

when employed alone, but no data were presented for its effect in mixtures with stronger pulping agents. Therefore, as a means of opening the problem for further investigation, the total reducing power of the liquor was used as the measure of chemical addition. The total reducing power toward iodine was 5.806 equivalents per charge of wood.

The results of these cooks are given in Table V and presented graphically in Figure 6.

TABLE V

COOKS WITH LIQUOR OF CONSTANT REDUCING POWER

| Cook | 1 | 2 | 3 |
|---|---|---|---|
| $Na_2S_2O_3$, g. | - | 178 | 218 |
| Brightness, % | 44.4 | 38.9 | 30.2 |
| Unscreened yield, % | 44.4 | 46.3 | 49.1 |
| Permanganate no. | 23.1 | 31.6 | 34.3 |

It is seen that the pulp brightness showed a definite decrease with successive cooks. However, it should be noted that the yield was constantly increasing, as was the permanganate number, which is a measure of the residual lignin in the pulp. Both of these factors are indicative of incomplete pulping. In fact, as shown in Figure 7, there appears to be a direct relation between pulp brightness and yield. There were two variables contributing to the decrease in pulp brightness: (a) less complete pulping of the stock—i.e., decreased lignin removal, and (b) a possible decrease in brightness caused by the effect of the cooking chemicals. It was the purpose of the next step to separate these variables so that the effect might be attributed to the proper source.

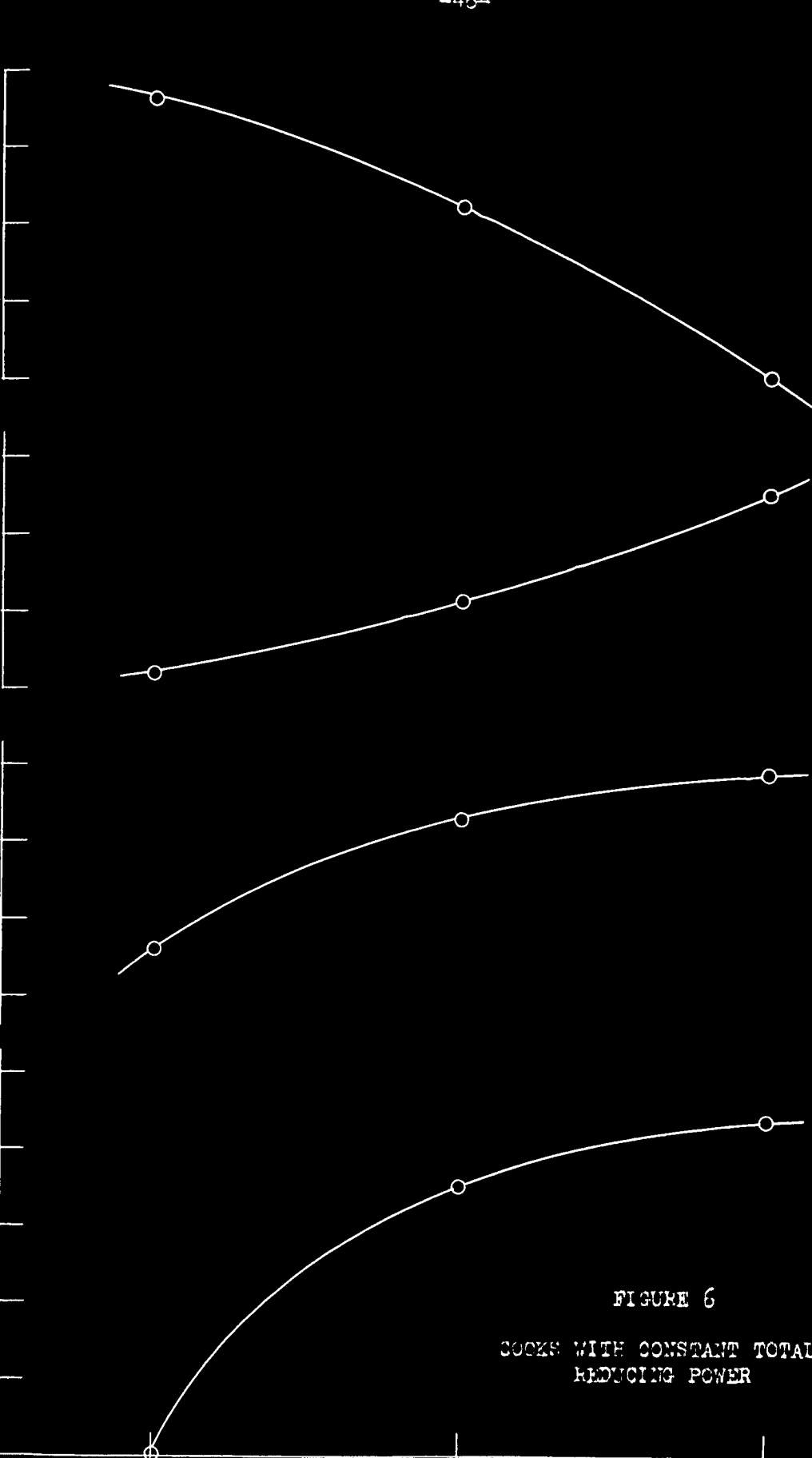


FIGURE 6

COCKS WITH CONSTANT TOTAL
REDUCING POWER

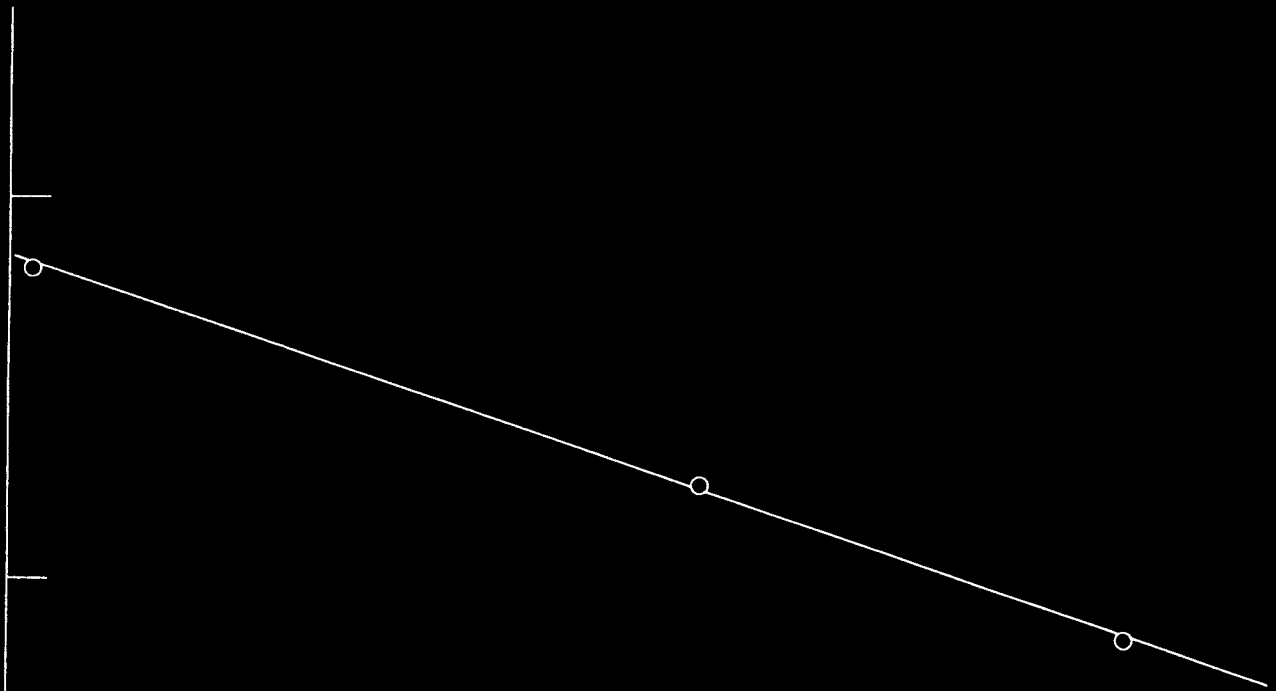


FIGURE 7

PULP BRIGHTNESS vs. UNSCREENED YIELD
(CONSTANT BLEACHING POWER)

EFFECT OF THIOSULFATE ON PULP QUALITY

This series of experimental cooks were carried out in groups of three cooks each. The purpose of this procedure was to give a spread in the pulp quality—for example, yield and permanganate number. Consequently, the three cooks made with the same cooking liquor for varying pulping times at maximum temperature, so that the resultant pulps exhibited a range in the completeness of the pulping operation. It was then possible to interpolate to a constant yield and arrive at a comparable pulping basis.

In contrast to the liquor composition described in the preceding section where the total reducing power was held constant, the liquor for each group was prepared so that the normal base demand of monosulfite was invariably present and, in addition, a certain amount of thiosulfate was present. The base demand of monosulfite (expressed as $Na_2O$) was arbitrarily designated as 100 per cent. The thiosulfate as $Na_2O$ was then expressed as a percentage of this chemical quantity. For example, a cooking liquor having 25 per cent thiosulfate would contain the base demand of 30 per cent monosulfite on the oven-dry wood and, in addition, 25 per cent of the monosulfite in the liquor as thiosulfate (all percentages are as $Na_2O$). In this way, sufficient chemical for the normal pulping requirement was always known to be present. These liquors were made up in a carboy and were siphoned into digesters so that variations from this source were eliminated. The liquors were prepared from pure chemicals and adjusted to the requisite pH by the introduction of carbon dioxide, which converted some of the

monosulfite into bisulfite with the formation of an equivalent quantity of bicarbonate. The conditions prevailing at the conclusion of this process corresponded closely to those in the liquors prepared by the method employing sulfur dioxide as previously outlined.

The results of these cooks are shown in Table VI.

TABLE VI

EFFECT OF SODIUM THIOSULFATE IN COOKING LIQUOR

| Series | Thiosulfate % | Cooking Time hr. | Yield % | Brightness % | Permanganate No. |
|---|---|---|---|---|---|
| Base Cook | 0 | 6 | 50.5 | 46.3 | 30.3 |
| A | 13.9 | 4 | 58.5 | 44.5 | 36.6 |
| | | 5 | 55.0 | 47.3 | 36.0 |
| | | 6 | 52.0 | 47.8 | 29.5 |
| B | 42.2 | 4 | 58.3 | 42.6 | 35.9 |
| | | 6 | 51.7 | 45.0 | 32.6 |
| | | 8 | 46.3 | 45.8 | 23.0 |
| C | 82.3 | 4 | 61.0 | 40.3 | 37.2 |
| | | 6 | 52.3 | 40.6 | 34.0 |
| | | 8 | 47.3 | 38.4 | 27.6 |
| D | 118 | 4 | 63.8 | 37.6 | 37.1 |
| | | 6 | 56.2 | 37.1 | 35.5 |
| | | 8 | 48.4 | 33.7 | 29.5 |

The brightness versus the unscreened yield has been plotted in Figure 8, and a smooth curve has been constructed between the points corresponding to the same liquor. It will be noted that the brightness increases with decreasing yield when the quantity of thiosulfate is low. This is the expected trend because, as the yield is reduced through a more complete solution of lignin, the brightness of the residual fibers would be expected to increase. However, as the concentration of thio-

Series A
Base Cook
Series B

sulfate in the liquor is increased, the brightness versus yield curve shows a maximum; this is particularly evident in Series C and D. An explanation for this phenomenon can be found if one considers the work of Aronovsky, who stated that, with more complete pulping, the pulp produced by sodium thiosulfate became progressively darker in color. Evidently, the inflection point on these curves with high concentrations of thiosulfate is the point at which the pulping action of this compound is initiated. Therefore, it may be concluded that sulfite reacts with the wood before the thiosulfate, and its action leads to increased pulp brightness with increased pulping. Thiosulfate, on the other hand, does not react with the wood as readily and eventual reaction causes a dulling of the pulp.

Evidently, there is a definite concentration ratio between these two chemical compounds at which the thiosulfate reacts sufficiently to produce a marked change in the resultant pulp. This may be stated on the basis of the relation between the maximum in brightness and the unscreened yield. In Series D (118 per cent thiosulfate), the maximum occurs at a yield of more than 60 per cent; in Series C (82.3 per cent thiosulfate), it occurs at a yield of approximately 56 per cent; with lower concentrations, the maximum was not attained, but it is assumed that it would appear below the experimental range. These results indicate that a certain amount of monosulfite must react and consequently be removed from the solution before the thiosulfate reacts appreciably. The mechanism for this phenomenon might be explained on the basis of the concentration of the reacting substance. Thus, with a large quantity of sodium thiosulfate present, the reaction is

initiated sooner and proceeds more rapidly as a consequence of mass action; as a result, less sulfite must be removed before its concentration is sufficiently decreased, with the resultant decrease in reaction velocity, so that the thiosulfate concentration and reaction velocity predominate. With higher thiosulfate concentrations, obviously less monosulfite must be removed and less wood reacted before the thiosulfate reaction is initiated.

Similar curves may be drawn from the permanganate number-brightness relationship as shown in Figure 9. The same maxima exist, and the same conclusions may be drawn with reference to the lignin residue as determined by the permanganate numbers.

When a line was constructed through the curves corresponding to the yield or permanganate number obtained in the base cook, it was possible to read the brightness which would be obtained with a pulp having the same yield or permanganate number as the standard. A curve could then be plotted showing the effect of additions of thiosulfate to the liquor at a constant pulp quality. These results are given in Table VII. It was also possible by this method to determine the cooking time at maximum temperature necessary to attain the desired condition; these results are likewise shown in Table VII.

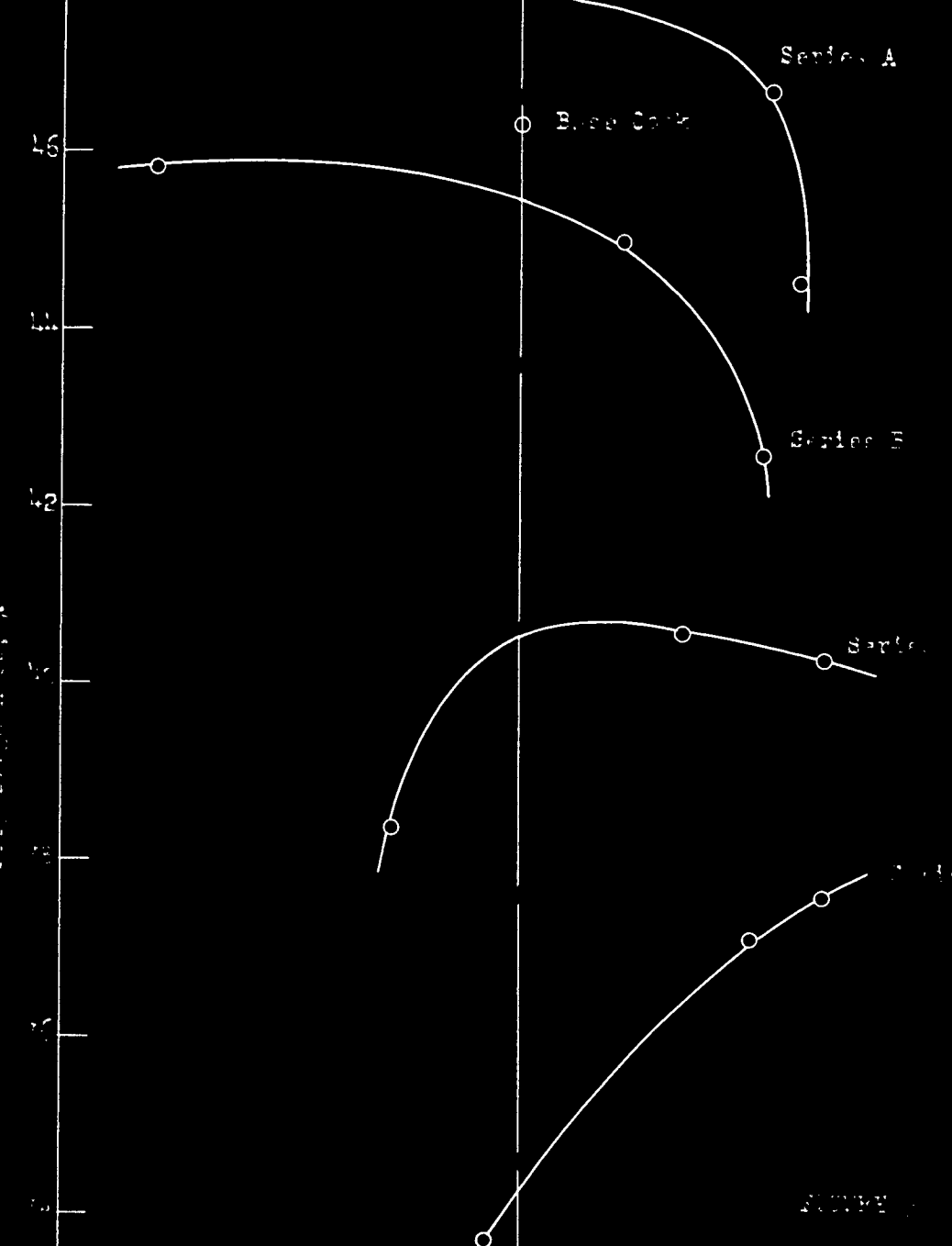

Series A
Base Case
46
44
42
Series B

TABLE VII

PULP BRIGHTNESS AT CONSTANT PULP QUALITY
AND TIME REQUIRED TO ATTAIN THIS QUALITY

| Thiosulfate % | Constant Yield Brightness % | Constant Yield Time hr. | Constant Permanganate Number Brightness % | Constant Permanganate Number Time hr. |
|---|---|---|---|---|
| 0 | 46.3 | 6 | 46.3 | 6 |
| 13.9 | 47.8 | 6.5 | 47.7 | 5.8 |
| 42.2 | 45.3 | 6.4 | 45.6 | 6.4 |
| 82.3 | 40.0 | 6.7 | 40.6 | 7.1 |
| 118.0 | 35.0 | 7.4 | 34.3 | 7.7 |

These results are shown in Figures 10 and 11. It is evident that pulp brightness is decreased by increasing additions of thiosulfate. The results also indicate that the reaction is slowed by increasing quantities of thiosulfate. A probable explanation for this is the fact that, when the liquor penetrates the chips, the thiosulfate and sulfite enter simultaneously; however, the sulfite reacts rapidly, leaving a high thiosulfate concentration in the interior of the chip which reacts very slowly and must diffuse from the chip to equalize the concentraton throughout the liquor before more monosulfite enters.

This theory is supported by visual observation of the pulped chips. Those cooked with liquors having high thiosulfate concentrations have hard uncooked centers which are very dark in color, whereas cooks made for the same length of time, but in which the thiosulfate was not present, are homogeneous throughout. Photographs in Figure 12 show this condition very clearly.

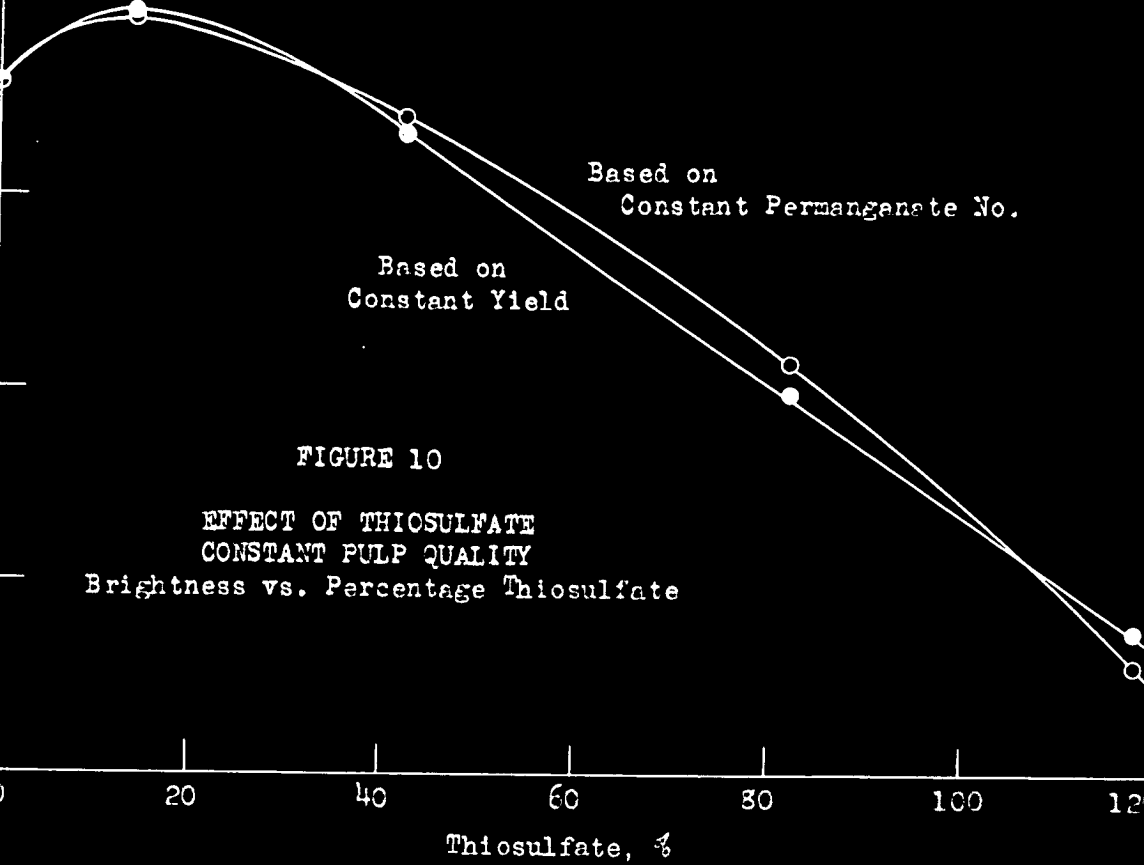



FIGURE 10

EFFECT OF THIOSULFATE
CONSTANT PULP QUALITY
Brightness vs. Percentage Thiosulfate

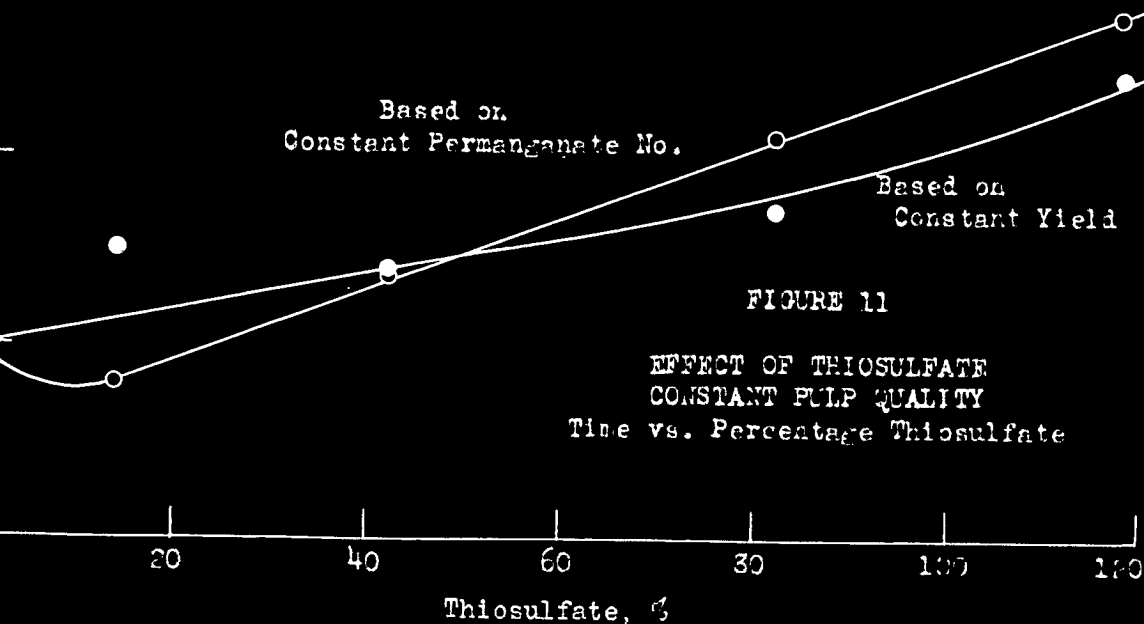
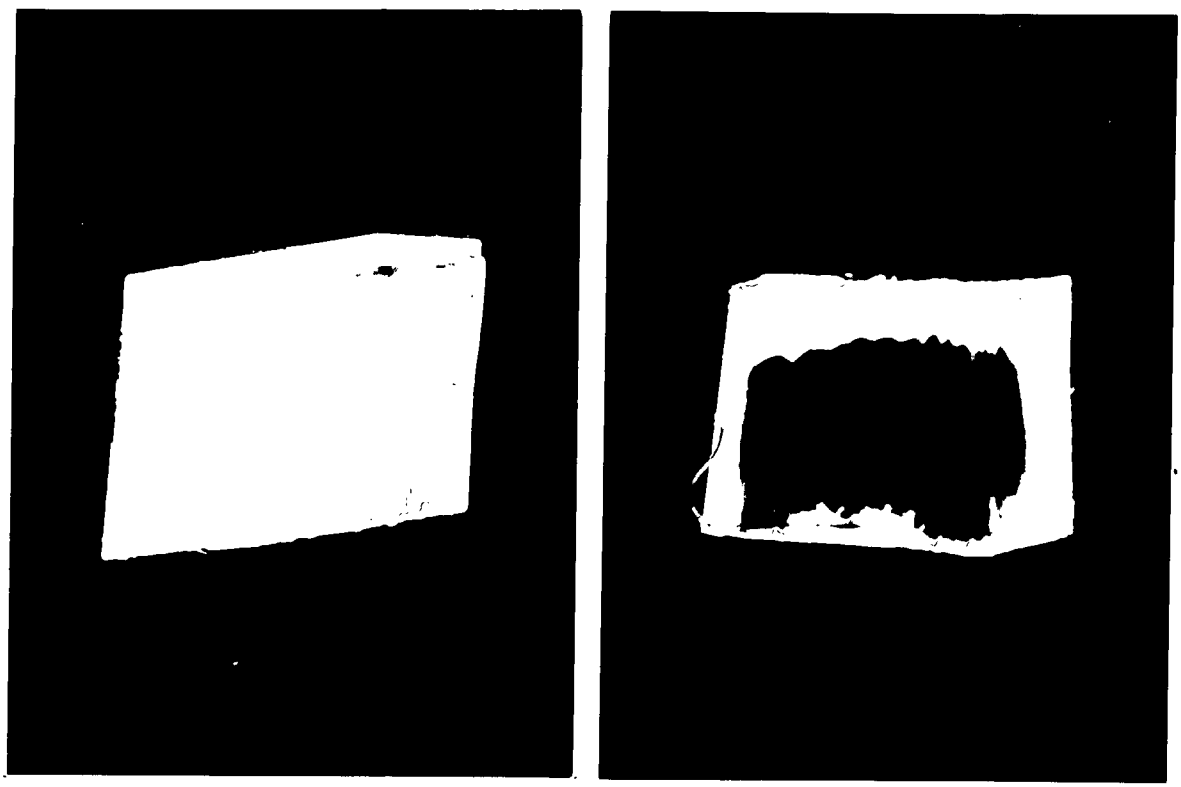



FIGURE 11

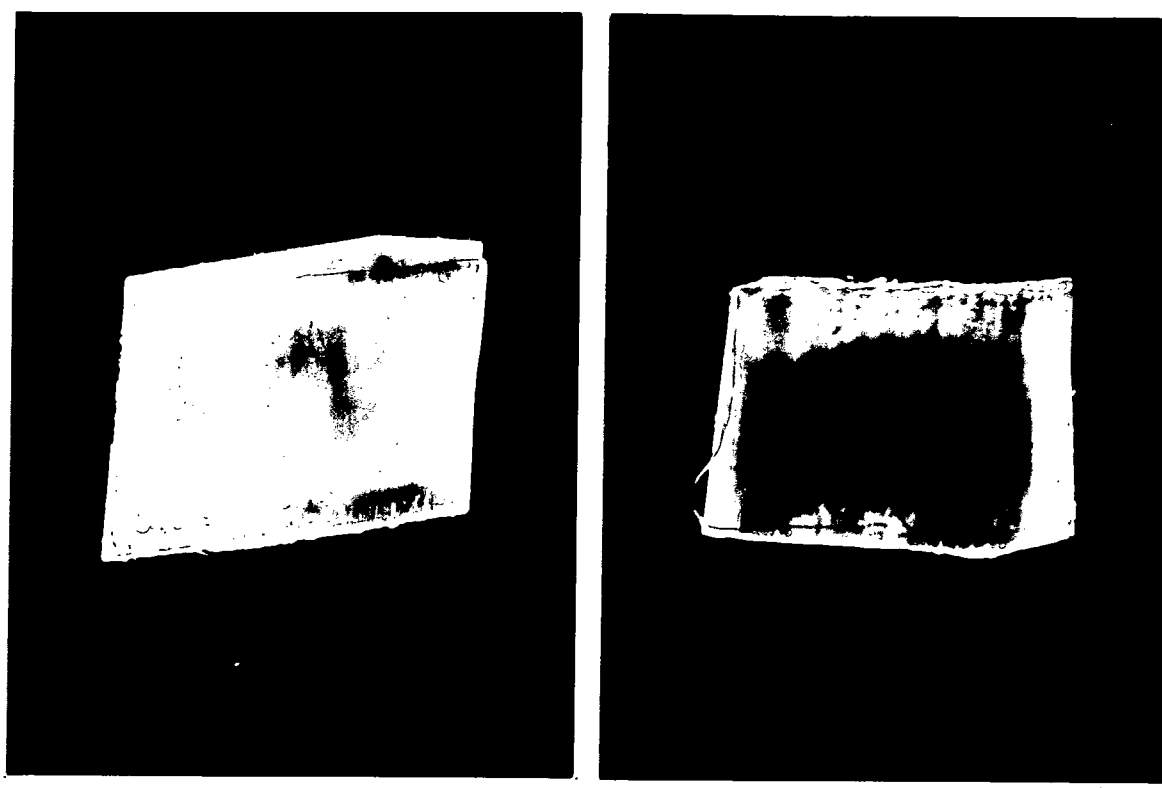
EFFECT OF THIOSULFATE
CONSTANT PULP QUALITY
Time vs. Percentage Thiosulfate



BASE COOK
4 Hours

82.3% THIOSULFATE
4 Hours

FIGURE 12



BASE COOK
4 Hours

82.3% THIOSULFATE
4 Hours

FIGURE 12

There is a slight increase in brightness over the base cook for the pulp obtained from liquor containing approximately 14 per cent of thiosulfate. This was accompanied by a decrease in permanganate number for the same cooking time. One explanation might be the fact that, although there is insufficient thiosulfate present to influence greatly the concentration of liquor in the chip or to alter the pulp brightness appreciably, the presence of the extra sodium salt increases the reaction rate by the common ion effect and the lignin removal is somewhat accelerated.

Lignin determinations were made on the pulps of Series B and D. It was hoped that in this way the correlation between the permanganate number and lignin residue could be established. As indicated in Figure 13, both series of cooks show excellent agreement and may be fitted into a smooth curve. The two pulp properties are directly related at lower lignin contents; however, at a permanganate number of about 32, the curve shows a break from linearity and its slope is so altered as to make the permanganate test less sensitive—i.e., a greater change in lignin content is required for the same increment of permanganate number than was the case in the linear region. The explanation for this is that, in the latter case, the excess of oxidizing material was reduced so markedly that the concentration change decreased the reaction velocity and, therefore, higher lignin contents were required to effect consumption of the permanganate.

Although the pulps cooked with varying quantities of thiosulfate showed good agreement, the base cook did not lie on this curve

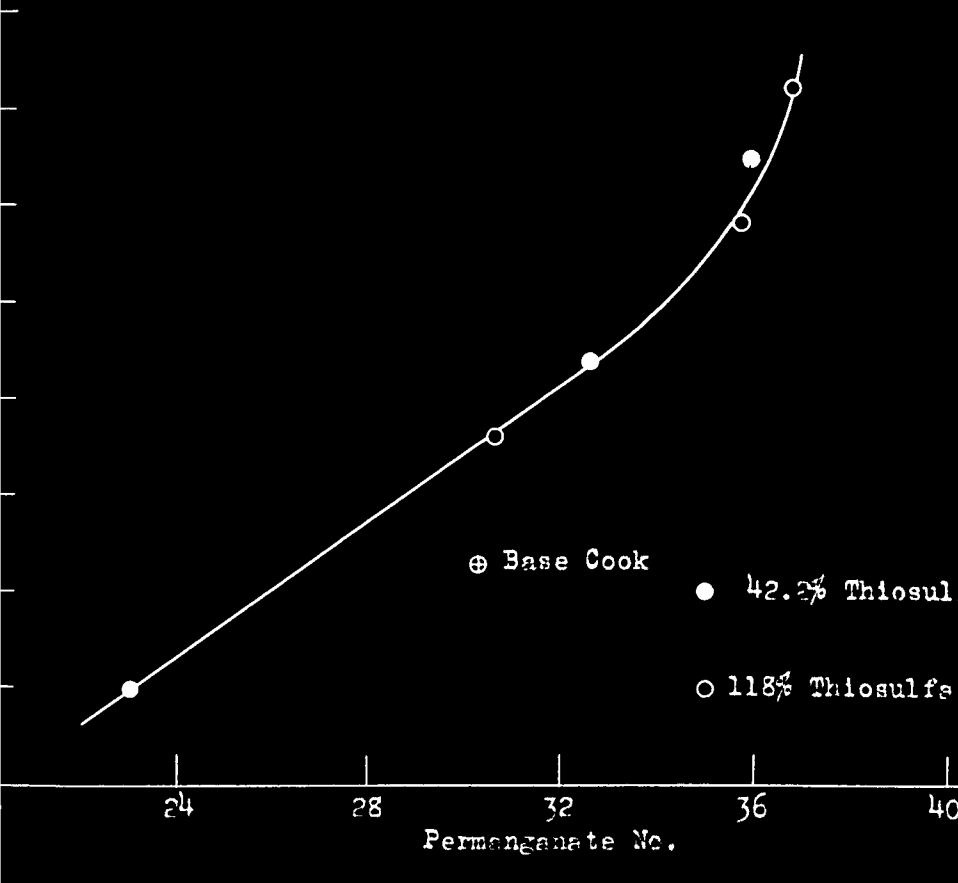



FIGURE 13

PERCENTAGE LIGNIN vs. PERMANGANATE NO.

but indicated a greater permanganate consumption than might be expected from its lignin content with reference to the previous results. Evidently, the correlation is true only for the same type of pulps. This limitation has no bearing on the previous discussion in which permanganate number was a good indication of lignin content.

FURTHER STUDIES ON THE EFFECT OF LIQUOR COMPOSITION

In order to study the effect of the recovery process more specifically, it was necessary to eliminate variations in the composition of the cooking liquor. Under such conditions, any changes in the pulp properties could be attributed to the smelting operation. Accordingly, a sulfide-carbonate solution was prepared from pure chemicals; this solution contained 20 per cent of the total chemical as sulfide. By sulfiting, the cooking liquor for Cook 101 was prepared from this mixture; after analysis, the liquor was used in a cook and data were obtained as shown in Table VIII. The waste liquor resulting from this cook was recovered and smelted.

TABLE VIII

REPEAT COOKS ON RECOVERED LIQUOR

| Cook | Liquor Analysis (Grams as $Na_2O$ per Digester Charge) Thiosulfate | Sulfide | Sulfite | Yield % | Brightness % | Permanganate No. |
|---|---|---|---|---|---|---|
| Base | — | — | 180 | 50.5 | 46.3 | 30.3 |
| Control | 99 | — | 180 | 52.0 | 41.6 | 32.6 |
| 101 | 103 | 9.4 | 180 | 52.8 | 27.5 | 33.8 |
| 102 | 103.8 | 6.9 | 180 | 54.1 | 26.3 | 36.5 |

The green liquor obtained from the smelting operation was found, on analysis, to be essentially a sulfide-carbonate mixture containing about 50 per cent of the total chemical as sulfide. This liquor was made to correspond to the original sulfide-carbonate solution by the addition of sufficient reagent sodium carbonate to produce a sulfide content of 20 per cent. The adjusted mixture was then sulfited to prepare the cooking liquor for Cook 102. The analytical results on liquors from Cooks 101 and 102 are in good agreement. There is a slight decrease in pulp brightness with the recovered liquor; however, this drop is small compared with that observed between these cooks and the control and base cooks (Table VIII). The control cook was made with liquor prepared from reagent sodium sulfite and thiosulfate so adjusted that the ratio between these constituents corresponded closely to that existing in Cooks 101 and 102. The base cook, of course, employed only reagent sodium sulfite. In both cases, the liquor was adjusted to the proper pH by the introduction of carbon dioxide.

Additions of sulfide to the cooking liquors were made in order to study its effect on pulp brightness. The range of these additions corresponded to the composition of cooking liquors from Cooks 101 and 102. A sulfite-thiosulfate solution of suitable ratio between constituents was first prepared and adjusted to the proper pH by the introduction of carbon dioxide. A separate solution of sodium sulfide was then prepared and adjusted to the proper pH by the introduction of hydrogen sulfide. After analysis, calculated aliquots of this solution were added to the sulfite-thiosulfate solution to produce liquors for Cooks 201, 202, and 203 (Table IX).

TABLE IX

EFFECT OF SULFIDE ADDITION

| Cook | Liquor Analysis (Grams as $Na_2O$ per Digester Charge) Thiosulfate | Sulfite | Sulfide | Yield % | Screenings g. | Brightness % |
|---|---|---|---|---|---|---|
| 201 | 98 | 180 | 5 | 49.5 | 30 | 39.9 |
| 202 | 98 | 180 | 10 | 50.4 | 52 | 39.8 |
| 203 | 98 | 180 | 15 | 50.2 | 59 | 37.1 |

Although the brightness decreased with increasing sulfide additions, the change was very slight in comparison with the changes observed in Table VIII. The yield was essentially constant and somewhat lower than previously attained; however, the screenings showed an increase with increasing sulfide, which at constant yield indicates decreased penetration into the chip.

In order to check these pulps for extraneous materials to which these dulling effects might be attributed, the pulps were analyzed for total sulfur and iron (Table X).

TABLE X

IRON AND SULFUR ANALYSES

| Cook | Ash % | Iron p.p.m. | Total Sulfur % |
|---|---|---|---|
| Base | 1.50 | 3.4 | 0.52 |
| Control | 1.51 | 8.5 | 0.55 |
| 101 | 1.32 | 5.0 | 0.34 |
| 102 | 1.50 | 6.8 | 0.47 |

There are no apparent trends except that the sulfur content has the same order as the ash content. This is also true of the iron content, except for the base cook. However, all of the values are extremely low, well within the expected values for the average commercial pulp. The differences in ash content are probably caused by variations in the degree of pulp washing. Therefore, pulp dulling cannot be caused by either of these constituents.

## CONCLUSIONS

Material balances on the white and green liquors of the sodium monosulfite pulping process showed that the chemical composition of these liquors was accounted for by their content of sulfide, sulfite, sulfate, thiosulfate, and carbonate. The sulfur balance agreed to within 2.5 per cent; the discrepancy could be accounted for, in part, by the phenomenon of coprecipitation. The sodium balance showed poorer agreement, since the deviation between the total by analysis and the total by individual components amounted to 5 per cent. The carbonate determination, which is obtained by difference and consequently dependent on several other analytical determinations, was subject to increased error and probably was responsible for the decreased precision. However, on the basis of these balances, it was concluded that, within the limits of experimental error, the constituents of these liquors were accounted for in the compounds analytically determined.

Cooks made with liquors corresponding to recovered waste liquors and at a constant total reducing power showed a decrease in pulp brightness with successive recovery operations. However, the unscreened yield and permanganate numbers correspondingly increased—an indication of incomplete pulping. Hence, this pulp dulling might be attributed, in some measure, to less complete pulping.

Pulps at constant pulp quality showed a decrease in brightness with increasing concentration of thiosulfate in the cooking liquor. On the basis of the cooking time required to attain a constant pulp quality, it was concluded that thiosulfate decreases the reaction

velocity. A possible explanation was found in the fact that, as the liquor penetrated the chip, the sulfite-thiosulfate ratio was constant. However, the sulfite was consumed in the reaction with the wood and resulted in a high concentration of thiosulfate within the chip, which hindered to some extent the further diffusion of the sulfite into the wood. Thus, the reaction rate was decreased. Visual examination of the cooked chips gave further support to this theory.

It was concluded that the reaction of the sulfite proceeded more rapidly than that of the thiosulfate. The basis for this conclusion was the relation between brightness and pulp quality at different cooking times, for a given concentration of thiosulfate. For high concentrations of thiosulfate, these curves showed a maximum which was concluded to be the point at which the predominance of the sulfite reaction was initiated. The degree of completeness in cooking at which this maximum fell varied with the thiosulfate content and, hence, it was concluded that the existing thiosulfate-sulfite ratio of the liquor was the controlling factor.

The lignin determinations showed excellent agreement with the permanganate numbers of these pulps, although the thiosulfate content varied widely.

Variations in the composition of the cooking liquors, prepared respectively, from pure and recovered chemicals but involving the sulfiting operation, were eliminated by suitable techniques of liquor preparation. Pulps obtained from recovered liquors agreed closely in brightness with those from liquors prepared with pure chemicals similarly

sulfited. However, pulps obtained from liquors having comparable analyses, but prepared from suitable pure chemicals so that the sulfiting operation was unnecessary, had a much higher brightness. It was concluded that the source of the phenomenon of pulp dulling was the sulfiting operation rather than the smelting operation, if the liquor subjected to sulfiting contained appreciable quantities of sulfide. Since the sulfide originated in such liquors through the smelting operation, the effect was ordinarily observed only in liquors obtained through the use of recovered chemicals.

It was concluded, on the basis of analyses of iron and sulfur in the pulps, that these extraneous components had no relation to the phenomenon observed.

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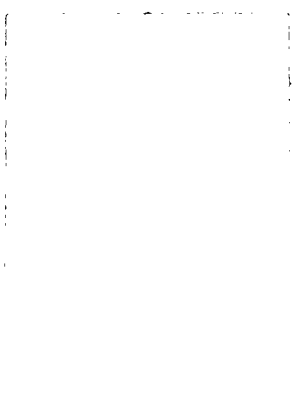
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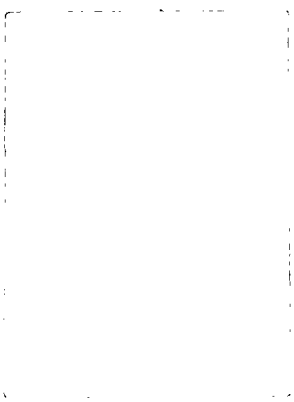
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Base Cook

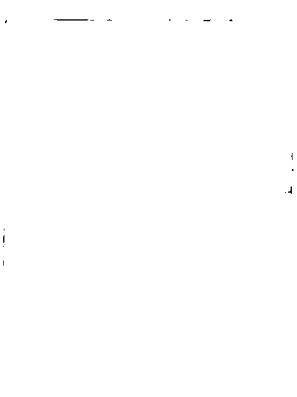
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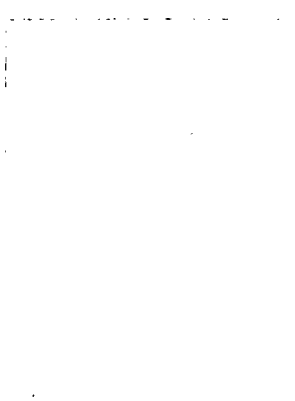
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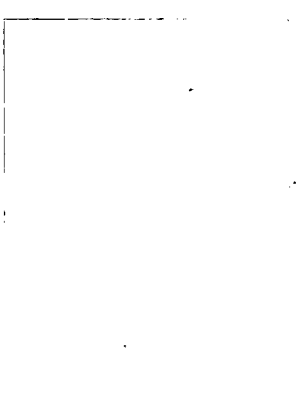
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Cook 201

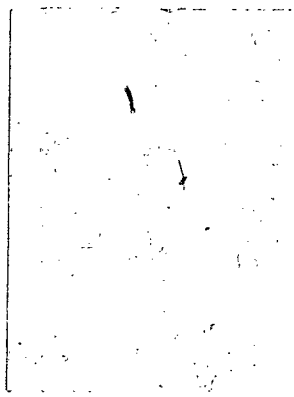


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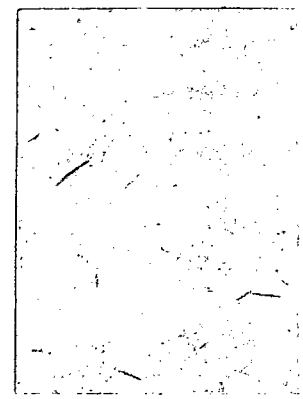


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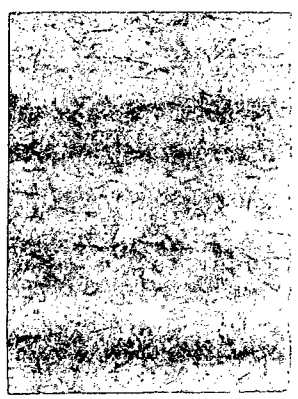
PULP SAMPLES



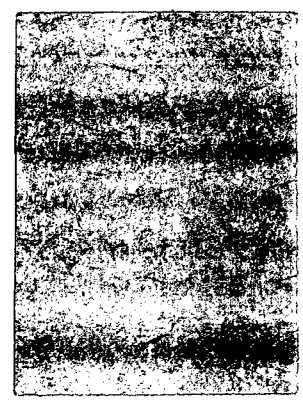
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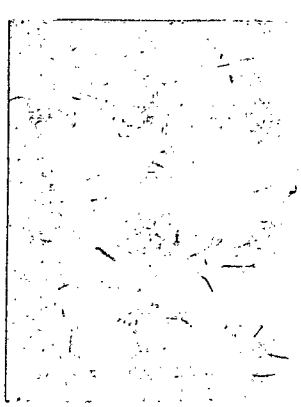
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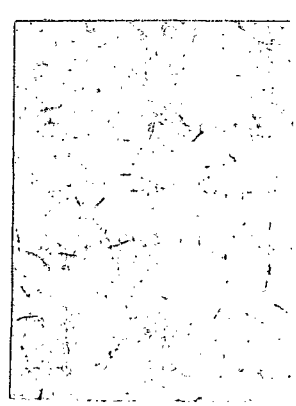
Cook 101



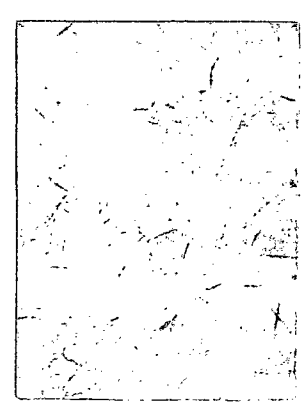
Cook 102



Cook 201



Cook 202



Cook 203

PULP SAMPLES