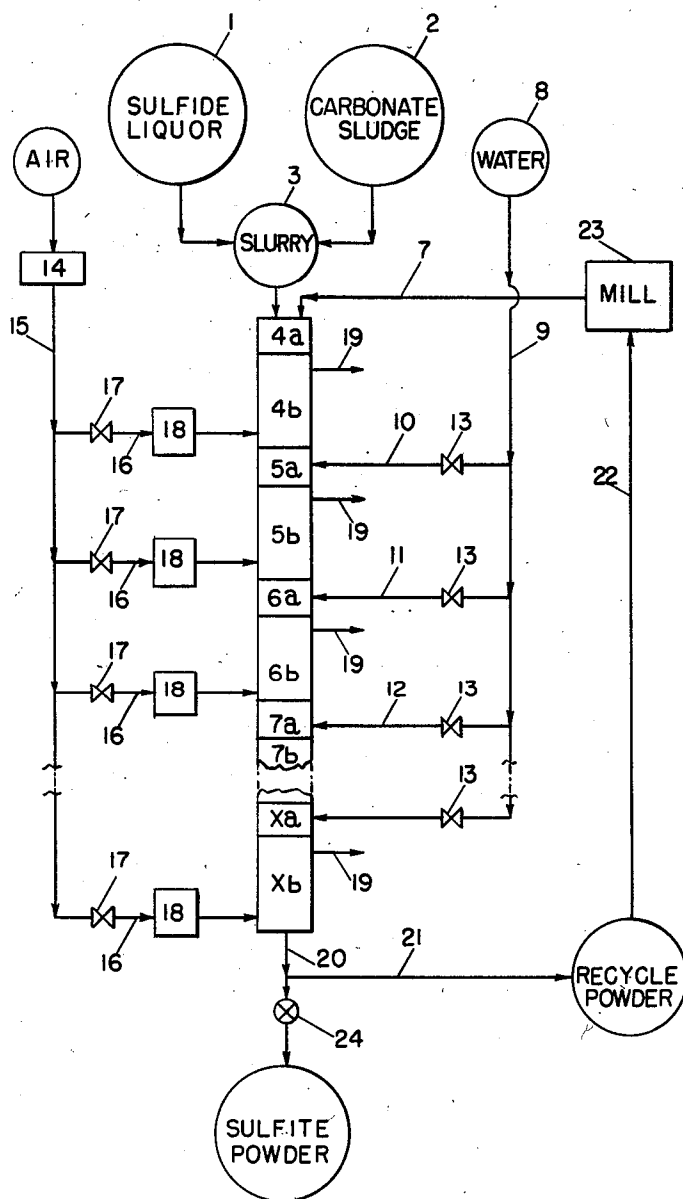


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METHOD OF OXIDIZING SODIUM SULFIDE TO
SODIUM SULFITE IN SUCCESSIVE STAGES
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METHOD OF OXIDIZING SODIUM SULFIDE
TO SODIUM SULFITE IN SUCCESSIVE
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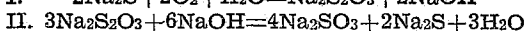
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This invention relates to an improved process for the oxidation of sodium sulfide to sodium sulfite and to improvements in the production of sodium sulfite for use in the neutral sodium sulfite cooking process for pulping fibrous vegetable matter from the waste liquors of the sulfate and neutral sodium sulfite cooking processes.

The lack of an economical process for recovering the chemicals of the neutral sulfite process has prevented the widespread adoption of this process, although the pulp made by this process is generally known to have outstanding strength and other desirable paper making qualities; and this is particularly true of pulp from low cost fibrous raw materials such as hard woods, canes, crops, grasses and other annual growths.

Proposals have been made to oxidize sodium sulfide, recovered from the green ash which results from the concentration, carbonizing and reducing of the waste liquors from the sulfate and neutral sodium sulfite processes, to convert it into sodium sulfite; but despite a well established need for such a process, no such process has been commercially available so far as we are aware. The principle difficulties encountered are those of handling the green liquor formed by the dissolving of the green ash in water, dusting losses and incomplete reactions. Residual quantities of sulfides and thiosulfates in the sodium sulfite formed are highly objectionable because of their deleterious action in the neutral sulfite pulping processes.

The reactions which are involved in the oxidation of sodium sulfide are the following:



Our investigations indicate that these are the only reactions which are involved. They are both highly exothermic, the first reaction producing about 348,000 B. t. u. and the second reaction about 593,000 B. t. u. per pound mole. The second reaction above converts only two-thirds of the product of reaction I into sodium sulfite, the remaining third reverting to sodium sulfide again, which must be oxidized once more by the mechanism of reaction I.

According to the present invention the oxidation of the sodium sulfide to sodium sulfite is carried out under carefully controlled conditions and with substantially complete oxidation of the sodium sulfide to sodium sulfite to give a sodium sulfite product free or substantially free from sulfide and from thiosulfate and which can be advantageously used in making cooking liquor

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for the neutral sodium sulfite cooking process.

We have found it advantageous to use concentrated sodium sulfide solutions for the oxidation and to mix them with enough inert powdered solids to yield a fluffy, discontinuous mass; and to effect stirring or tumbling of such mass in contact with air so that the oxygen of the air will diffuse rapidly through the film of liquid carried by the powdered solids. In order for the reaction to proceed at a reasonable rate all the sodium sulfide must have a good access to the comparatively large amount of air required for oxidation and we have found it advantageous to provide large interface areas and high rates of diffusion from the interface areas. Thick films of sodium sulfide were found to oxidize very slowly owing to their slow diffusion rate and we have found that when the films become viscous or dry the reaction stopped.

We have found that the heat of reaction generated at the temperatures at which the reactions take place tends to form a dry product and to stop the reaction.

We have found it important to add water to the partially reacted product in amount sufficient to redissolve the dried sodium sulfide which is formed by the second reaction and which would otherwise remain as an objectionable constituent of the product. The large amount of heat of reaction which, with the first reaction is sufficient to evaporate more than two pounds of water per pound of sodium sulfide and with the second reaction sufficient to evaporate about 1.8 pounds of water per pound of sulfide, tends to dry out the product and to stop the reaction. But by adding water in sufficient amount to redissolve the sodium sulfide of the dried out product the reaction can be continued to completion.

The reactions above indicated will take place at lower temperatures, around 250° F., but take place rapidly at temperatures around 275° F. If, however, the reaction temperatures are too high there is danger of oxidizing the sulfite formed to sulfate which is objectionable. In general the temperature of the process should not go above about 300° F. and is advantageously carried out within the range of around 275 to 295° F.

We have also found that the process can advantageously be carried out as a continuous process with the addition of regulated amounts of strong sodium sulfide solution with a large amount of inert powdered solids and with passing of the material through a series of zones with separate addition and cross-flow of air to the

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successive zones and with supplying of added water in the successive stages to redissolve the sulfide remaining or formed by the second reaction above and which has been dried out by the high temperature and heat of reaction.

We have found it advantageous to make use of a sodium sulfide solution containing about 3 to 4 pounds of water per pound of sodium sulfide and to use sodium sulfite crystals, or a mixture of sodium sulfite and sodium carbonate crystals as the solids on which the solution is spread as a thin film. We have found it advantageous to use solid particles for carrying the sulfide solution having a particle size of below about 700 microns and to avoid such extremely small particles as would tend to agglomerate into air-imperious masses or to escape with the air as dust.

We have also found it advantageous to use an amount of solution such that there is only about 10 pounds of water per 100 pounds of dry powder in order to keep the powder with its thin film of sulfide in a fluffy condition for aeration; and that with such a limited amount of water it is advantageous to use concentrated sodium sulfide solutions such as those above indicated; and to supply added water at later stages of the process to maintain sufficient water throughout the process to insure that the sodium sulfide formed is kept in solution or redissolved so that the reactions can again take place and be carried to completion.

It is also advantageous to supply the air in successive installments at successive stages of the process. By proceeding in this way the reactions can be advantageously controlled and the loss of product by dusting minimized, whereas, if all the air must pass over or through all of the powder, there is danger of dusting, particularly where the powder has become dry. The separate addition of air at successive stages and at low velocity minimizes dusting and insures fresh air at successive stages of the process.

In carrying out the process, and allowing about 100% excess air for the oxidation, one pound of sodium sulfide, mixed as a solution with about 30 pounds of powder, is oxidized by about 100 cubic feet of air at a temperature around 300° F. In a unit required for a 100 ton per day pulp mill, about 15 pounds per minute of sodium sulfide must be oxidized; and this requires an air rate of around 1500 cubic feet per minute; and with a period of about 1 hour required for the aeration and oxidation, this would mean around 90,000 cubic feet of air passing over the powder. But by dividing up this air and supplying it at a series of successive stages and with cross-flow of the air the oxidation reaction can be kept under control and the loss of valuable product by dusting minimized.

The present process is advantageously carried out in a continuous manner by recycling the hot sulfite product and using it as a carrier for the freshly added concentrated sodium sulfide solution. By recycling the hot powder in this way continuously and continuously adding sulfide to it and withdrawing an equivalent portion of the powder as a reaction product, the process is a continuous one with a continuous oxidation of sulfide and forming of sulfite. The use of the hot recycling sodium sulfite, after crushing to break up any lumps that may be formed, serves to preheat the concentrated sodium sulfide solution which is added to it and spread over it in the form of a thin film, thus promoting the start

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of the reaction. The concentrated sodium sulfide solution can also advantageously be preheated before adding it to the solid powder.

An arrangement of apparatus which can advantageously be used in carrying out the present process, is shown in the form of a flow sheet on the accompanying drawings.

A supply of sulfide liquor is indicated at 1 and this liquor is advantageously in the form of a concentrated solution containing around 3 to 4 pounds of water per pound of sodium sulfide and may advantageously be hot or preheated liquor. A sodium carbonate sludge product is indicated at 2 which may be admixed with the sulfide liquor to form a slurry indicated at 3; or the sulfide liquor can be used without admixture of carbonate sludge.

Sectionalized reaction apparatus in the form of a series of sections is shown conventionally in the drawing, each section being indicated as made up of two parts, 4a and 4b, 5a and 5b, etc. up to Xa and Xb, where X represents the number of successive sections.

A supply of sulfite powder is supplied through the line 7 to the first section 4a, where it is mixed with the sulfide liquor in proportions to form a thin film of solution on the sulfite particles. Where a carbonate slurry is admixed with the sulfide liquor the admixture of this slurry with the sulfite powder will be in proper proportions to form a thin film of the sulfide solution on the carbonate and sulfite crystals or particles.

The series of successive sections or compartments may be in the form of a sectionalized screw conveyor which will serve to keep the sulfide-coated powder in a state of agitation and insure contact with the air. The successive sections are supplied with water connections from the water supply 8 through the line 9 and the branch lines 10, 11, 12, etc., each having a metering and cut-off valve 13 therein so that a small controlled supply of water may be added at any of the successive stages or sections. Air is supplied by the blower 14 through the line 15 and the branch lines 16, each having a control valve 17 therein, and each shown as provided with a heater or preheater 18 for preheating the air to the desired temperature before introducing it into the successive stages of the apparatus. Exhaust or discharge connections 19 are provided for each section. The arrangement of the air supply and exhaust is such that each section is provided with its own supply of hot air which flows generally cross-wise through the successive sections.

The apparatus can be heated (by heating means not shown); or the hot sulfide liquor and sulfite may be in a hot state before admixture; and heat can also be supplied with the air entering each section.

The finished sulfite product is discharged from the last section through the line 20 and a large part of this is advantageously recycled as recycle powder through the lines 21 and 22 and passed through the mill 23 to break up any lumps and is then returned through the line 7 as the sulfite powder which serves as a carrier for the sulfide solution.

The arrangement shown on the drawings is schematic or diagrammatic and in practice the discharge from the last section may be located in close proximity to the first section so that the hot sulfite powder discharged from the apparatus is recycled and returned in a hot state for admixture with the sodium sulfide solution. A por-

tion of the final sulfite powder equivalent to the sodium sulfide liquor added or to the slurry of sulfite liquor and carbonate sludge added is withdrawn through the line 24.

In such a sectional apparatus through which the material is passed successively and maintained in a state of agitation, the reactions involved in the oxidation of the sulfide at elevated temperatures take place with supply of air successively at different stages and supply of water at successive stages as required to maintain the sodium sulfide in solution and to redissolve any dried out product so that the reaction can go to completion. In other types of apparatus than a screw conveyor type such as a long single kiln or mixer provision can similarly be made for water distribution inlets at successive intervals and for successive additions of air and cross-flow of air through successive sections.

In the continuous operation of the process the amount of water required at successive stages can readily be determined by examination of a sample of the material at the different stages and supplying water where required to the dried-out product to insure redissolving of dry sulfide and further progress of the reactions. The water can be added as a fine spray in regulated amount. Water can also be added with the air or with part of the air at one or more successive stages of the process. Mixtures of air and steam can also be used to inhibit the complete evaporation of water. Where the surface film has dried out, the addition of water should be sufficient to redissolve the sulfide contained therein. But by careful regulation of the addition of water the sulfide originally present and that subsequently formed can be kept in solution throughout the process; thereby accomplishing much the same result as where water is added to redissolve sulfide after the surface film has become dry.

By supplying water as required at successive stages of the process and by supplying heat as required at successive stages the process as a whole can readily be kept under control and strong initial sodium sulfide solutions used and objectionable drying out of the product and stopping of the reaction avoided. The supply of water also prevents overheating or excessive heating of the reaction mixture due to exothermic heat of reaction.

The sulfite product produced by the oxidation process, when properly controlled, is free or substantially free from both unoxidized sodium sulfide and from sodium thiosulfate and contains a minimum amount of neutral sodium sulfate from over-oxidation of the sulfite produced. Where sodium carbonate sludge is admixed with the sulfide liquor the product will be a mixture of sodium sulfite and sodium carbonate and the recycled powder will be a similar mixture.

The sulfite product produced by the process, or the mixture of sulfite and carbonate, can advantageously be used for the production of cooking liquors for the neutral sodium sulfite process, by subjecting any admixed carbonate to partial sulfiting with SO_2 to give a neutral sulfite cooking liquor with a desirable content of sodium carbonate.

A typical product of the oxidation process above described made from a slurry of sodium sulfide solution and sodium carbonate, produced by dissolving the green ash from the neutral sulfite black liquor may thus contain around 36 mole percent sodium sulfite, 5 mole percent sodium sulfate and 59 mole percent sodium carbonate.

Such a product can readily be dissolved to form a solution of 10 to 20% of dissolved salts; with added sodium carbonate as required to make up for losses and this solution can then be sulfited to the desired degree by passing it through a tower in contact with sulfur dioxide gas and stopping the sulfiting before all of the sodium carbonate is converted to sodium sulfite. A cooking liquor may thus contain from 1 to 3 equivalent proportions of sodium carbonate or bicarbonate to 10 equivalent proportions of sodium sulfite.

The concentrated sodium sulfide liquor which is admixed with the finely divided solid carrier in carrying out the present process is advantageously that produced by continuously adding the hot, molten green ash (from the waste liquor of the sulfate or neutral sodium sulfite pulping process) to a large body of concentrated sodium sulfite solution containing sodium carbonate in suspension, with corresponding addition of fresh water to dissolve the added sodium sulfide without dissolving any appreciable amount of the sodium carbonate; and continuously drawing off a portion of the resulting suspension of sodium carbonate in sodium sulfide, settling out the sodium carbonate sludge and returning part of the clear sodium sulfide solution to the large body to which the molten green ash is added, while drawing off the excess of concentrated sodium sulfide produced. The sodium carbonate sludge separated in such process may be admixed in desired proportions with the concentrated sodium sulfide solution for use in the present process; or the strong sodium sulfide solution can be used alone, without the carbonate sludge, in the present process. This method of forming such a concentrated sodium sulfide solution and a sodium carbonate sludge from the green ash of the sulfate or neutral sodium sulfite waste liquor treatment is more fully described in our companion application Serial No. 77,934, filed February 23, 1949.

We claim:

1. The method of oxidizing sodium sulfide to sodium sulfite in successive stages which comprises mixing a concentrated sodium sulfide solution with inert powdered solids to form a fluffy, discontinuous mass, agitating and aerating the mass at an oxidizing temperature of about 250° F. to 300° F. to effect oxidation of sodium sulfide, and continuing the agitation and aeration and adding sufficient water to the mass to keep the unoxidized sodium sulfide in solution during the later stages of the oxidizing treatment.

2. The process according to claim 1 in which water is added with the air in amount sufficient to keep the sodium sulfide in the dissolved state until oxidized to sulfite.

3. The process according to claim 1 in which the aeration is effected at successive stages by separate additions of air and separate withdrawal of the spent air from the successive stages.

4. The method according to claim 1 in which a portion of the hot sodium sulfite resulting from the oxidation is returned and admixed in a hot state with the concentrated sodium sulfide solution to form the mixture subjected to the oxidizing treatment.

5. The method of oxidizing sodium sulfide to sodium sulfite which comprises mixing a concentrated sodium sulfide solution with inert, powdered solids, mainly sodium sulfite, to form a fluffy, discontinuous mass, passing this mass successively through a series of separate zones at an oxidizing temperature of about 250° F. to

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300° F. and agitating and aerating the mass in each of said zones to effect oxidation of the sodium sulfide, introducing air for aeration to the successive zones with cross-flow of the air through the successive zones and adding water to maintain unoxidized sodium sulfite in solution in the later zones of the oxidizing treatment.

6. The method of oxidizing sodium sulfide to sodium sulfite in successive stages which comprises mixing a concentrated sodium sulfide solution with inert powdered solids to form a fluffy, discontinuous mass, agitating and aerating the mass at an oxidizing temperature of about 250° F. to 300° F. to effect oxidation of sodium sulfide, adding water to the partially oxidized mass to

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maintain sodium sulfide in solution during the later stages of the oxidizing treatment, and continuing the agitation and aeration to effect substantially complete oxidation of sulfide and to give a product substantially free from sodium sulfide and sodium thiosulfate.

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