My present invention relates to an improved method of converting sodium sulfide to sodium sulfite. More particularly it relates to an improved method of converting so-called "smelt liquor" containing essentially sodium sulfide and sodium carbonate to liquor containing essentially sodium sulfite suitable for cooking wood by the so-called monosulfite method.

This method of pulping has long been proposed but its use has been limited because of difficulties in the recovery of sodium and sulfur values in the waste liquor. In most instances the waste liquor has been discarded, thereby creating a stream pollution problem, or utilized in the recovery system of a Kraft mill where such mill happens to be conveniently adjacent. When the waste liquor is concentrated and burned, the sulfur present is reduced to the sulfide, thereby posing the problem of converting the sulfide to the sulfite. Many proposals have been made to this end. These may be divided into at least five general categories, viz., precipitation of insoluble sulfides; direct oxidation of the smelt solutions; electrolysis; ion exchange; and, finally, liberation of the sulfur as hydrogen sulfide and its subsequent disposition either by oxidation or otherwise.

Except for some of the methods involving electrolysis and ion exchange, those names require concentration and burning of the waste liquor.

My present method relates to the last named, i.e., that involving the liberation and subsequent oxidation of hydrogen sulfide. It also involves an initial carbonation of the smelt liquor which operates to release the sulfur, combined as sodium sulfide, as hydrogen sulfide. Most of the heretofore proposed methods which involve the formation of hydrogen sulfide require the burning of it to sulfur dioxide. It will be observed that in carrying out such methods an excess of carbon dioxide must be employed in order for it to act as a stripping agent to carry from the solution the formed hydrogen sulfide. Now when the mixture of carbon dioxide and hydrogen sulfide is burned, a gaseous mixture is obtained consisting essentially of the carbon dioxide originally present, the sulfur dioxide formed by the air oxidation of the hydrogen sulfide and the large volume of nitrogen remaining from the air oxidation. Thereby a mixture is had which because of its great volume requires equipment of extreme size and of high cost to handle it. Furthermore the corrosive quality of the gaseous mixture adds to the difficulty. Nevertheless for the process to be commercially feasible, the sulfur values must be recovered to a substantial degree.

My invention is predicated upon my discovery that the above type of recovery method may be greatly simplified and improved by establishing a closed gas cycle in which a recycled stream of carbon dioxide will perform the following functions:

1. Of acting as the carbonating agent for the smelt liquor;
2. Of acting as the stripping agent for the hydrogen sulfide with elimination of substantially all of the sulfide sulfur from the carbonate solution;
3. After the removal of the hydrogen sulfide as elemental sulfur by reaction with sulfur dioxide, preferably in the form of sulfuric acid, of acting as a stripping or desorbing agent for a sufficient quantity of sulfur dioxide from its solution in water whereby the mixture may be used as the sulfiting agent for the carbonates formed in the sulfiting step with the release of substantially pure carbon dioxide which is immediately available for carbonating in the commencement of a new cycle. The elemental sulfur formed is readily separated, burned to sulfur dioxide, and the latter recovered as sulfuric acid for the subsequent oxidation of the hydrogen sulfide. In this manner what amounts to a closed acid cycle is combined with a closed gas cycle. The excess carbon dioxide may be vented from the system as required.

My improved method involves the following known reactions:

1. \( \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow 2\text{NaHCO}_3 \)
2. \( \text{Na}_2\text{S} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow 2\text{NaHCO}_3 + \text{H}_2\text{S} \)
3. \( 2\text{H}_2\text{S} + \text{H}_2\text{SO}_3 \rightarrow 3\text{S} + 3\text{H}_2\text{O} \)
4. \( \text{H}_2\text{SO}_3 + \text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 \)
5. \( 2\text{NaHCO}_3 + \text{H}_2\text{O} + \text{Na}_2\text{SO}_3 + 2\text{CO}_2 \rightarrow 2\text{H}_2\text{O} + \text{Na}_2\text{SO}_4 + 2\text{Na}_2\text{CO}_3 \)
6. \( \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{Na}_2\text{SO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow 2\text{NaHCO}_3 \)
7. \( \text{SO}_2 + \text{O}_2 \rightarrow \text{SO}_3 \)
8. \( \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3 \)

Advantages which will be readily apparent are that the major equations involved, i.e., Nos. 2 and 5, readily go to completion with the result that no appreciable quantity of sulfide sulfur escapes reaction and no appreciable quantity of sulfur dioxide is admitted to the carbonation step. Offhand it might be supposed that the presence of sulfur dioxide in the carbonating column would merely anticipate the reaction which is carried out in the sulfiting column and hence would be without significance. However, to sulfite in the carbonating column would have the result of giving rise to large quantities of thiosulfates which represent a complete loss of useful sulfur. Such thiosulfates are formed according to the following reaction which easily goes to completion:

\( 2\text{Na}_2\text{CO}_3 + 2\text{Na}_2\text{SO}_3 + 2\text{SO}_2 + 3\text{H}_2\text{O} \rightarrow 3\text{Na}_2\text{SO}_4 + 2\text{Na}_2\text{CO}_3 \)

Substantially no sodium salts are lost and under the conditions obtaining for the oxidation of the H_2S formed, the loss of sulfur as polythionates is kept at a minimum. A further advantage is that the improved method may be carried out under atmospheric pressure and with a minimum of such steps as evaporation, precipitation and filtration. Since no air is admitted to the sulfiting column, there is no tendency to form sulfates. Other advantages will be apparent as the description proceeds and the features of novelty will be pointed out in the appended claims.

The invention will be best understood by reference to the following detailed description taken with the annexed drawings in which:

Fig. 1 is a process flow diagram of a preferred embodiment;
Fig. 2 is a somewhat diagrammatic showing of a plant for carrying out the process shown in Fig. 1.

For sake of brevity, the following chemical symbols will be used in lieu of the names of the more frequently referred to chemical compounds involved in the process:
for carbon dioxide, CO_2; for sulfur dioxide, SO_2; for hydrogen sulfide, H_2S; for sulfuric acid, H_2SO_4; for sodium sulfide, Na_2S; for sodium sulfate, Na_2SO_4; for so-
dium monocarbonate, NaCO₃; for sodium bicarbonate, NaHCO₃.

A brief description of the method will first be given followed by specific examples of quantities of materials used, reference being had to Fig. 2. Smelt liquor is introduced through pipe 9 into the carbonating column 10 counter-current to a stream of substantially pure CO₂ introduced at the bottom thereof through the pipe 11. The carbonation as represented by Equations 1 and 2 takes place and the excess CO₂ sweeps with it the formed H₂S out the top of the column through pipe 12 through which it is conveyed to the bottom of column 13 which is the sulfur oxide column and stripping column. Normally the H₂S formed will be about 10% of the mixture of CO₂ and H₂S, i.e., 7 moles of CO₂ to one mole of H₂S. There the H₂S meets the H₂S₀₂ introduced into the top thereof through pipe 14 and in the column the oxidation of the H₂S to elemental sulfur (Equation 5) takes place. The slurry of sulfur and water which is formed leaves the bottom of the column through pipe 15 and, aided by pump 16, is passed into the sulfur settling tank 16a. By having the H₂S₀₂ as nearly spent as possible at the bottom of the tower where it meets the incoming CO₂ and H₂S mixture, the polythionic acids formed further up the tower or elsewhere will be largely reduced to sulfur.

The CO₂ stream in column 13 desorbs some of the SO₂ and this mixture of CO₂ and SO₂ leaves the top of the column through pipe 17 and, aided by the blower 18, is introduced into the bottom of sulfuting column 19 in which it meets the sodium bicarbonate solution from column 10 which flows through pipe 20, pump 21, to the top of said column 19. Therein the sodium bicarbonate or monocarbonate present is converted to sodium sulfite substantially in accordance with Equation 5. An agitator 22 in column 19 serves the purpose of releasing dissolved CO₂ from the sulfited liquor; otherwise the dissolved gas may interfere with the subsequent pumping operation. The resulting sodium sulfite solution is the product of the system and leaves the column 19 through the pipe 22. The sulfur from the settling tank 16a is removed therefrom through pipe 23 to the dewatering press 24 and a more concentrated slurry leaves through pipe 25 by which it is conveyed to the sulfur melt tank 25a and thence to sulfur burner 26. Make-up sulfur is added to tank 25a through pipe 27. The products of the air oxidation of the sulfur pass through the column 28, the SO₂ removed by the action of water from tank 16a introduced into the column through pipe 29. The H₂S₀₂ formed leaves the bottom of column 28 by pipe 30, and aided by pump 31, passes through pipe 14 to the column 13. The amount of CO₂ used will in general be determined by that needed in the stripping column 13 since for the most part that required for stripping in said column will be little more than twice that required for carbonation. That needed in the stripping column is governed by the composition of the equilibrium mixture of the two gases, i.e., of CO₂ and SO₂, which is dependent on the partial pressure of SO₂ over the sulfurous acid. In this manner the CO₂ required is related to the concentration and temperature of the sulfurous acid, regard being had to the fact that as the temperature is raised the equilibrium partial pressure of the SO₂ is also raised so that when the SO₂ from the sulfur burner 26 is absorbed at the higher temperature a weaker acid is produced; on the other hand, a higher temperature will cause a greater amount of SO₂ to be desorbed by the CO₂ in the stripping operation. Lower temperatures are advantageous in unvoicing process losses.

The amount of SO₂ desorbed in sulfiting column 19 will bear a substantially stoichiometric relationship to the amount of sodium salts of carboxylic acid formed in the carbonating step, it being from Equations 5 and 6 that one mole of SO₂ is needed for each two moles of sodium present regardless of the amount of the carboxylic acid radical present. The excess CO₂ may if desired be carried along through the carbonator provided the column will accept so large a gas flow. Preferably a valve by-pass 32 is employed for the purpose of bypassing a portion of the CO₂. Where the amount of CO₂ increases beyond that needed as make-up for losses, as may happen during the operation of Equation 5, the excess is bled off through valve by-pass 34 to disposition not shown.

It will be noted that the concentration of the H₂S₀₂ is determined by the fact that it is obtained by passing the products of the air oxidation of sulfur through a scrubbing tower under atmospheric pressure. Under these conditions, the partial pressure of the SO₂ in the resulting solution is such as to limit the amount of dissolved SO₂ to a value of from 1 to 2% depending upon the temperature as above pointed out. Greater concentrations than this would result in an undesirably large amount of SO₂ being stripped from the solution and added to the gas cycle. Furthermore, by circulating a larger amount of water in the so-called acid cycle (see Fig. 1), the concentration of acid is lower whereas if a smaller amount of water is circulated, the concentration of acid is higher.

The pressure of the dewatering press 24 is optional; also it has been found of advantage to add a flocculating agent to the sulfur slurry to aid in its precipitation. Of such agents, alum (aluminum sulfate) has been used satisfactorily.

Example 1

In this example the smelt liquor from the pulping of one ton of wood is introduced to the column 10. This liquor has the following composition:

<table>
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<tr>
<th>Substance</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂S</td>
<td>180 lbs</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>180 lbs</td>
</tr>
<tr>
<td>Water</td>
<td>10,000 lbs</td>
</tr>
</tbody>
</table>

To run this amount of liquor, 2000 lbs of CO₂ is admitted through pipe 11. When the reaction is complete, 74 lbs of H₂S is formed and added to the 2000 lbs. of CO₂ leaving the top of the carbonating column through pipe 12. 332 lbs. of SO₂ in 33,600 lbs of water is introduced into the column 13 (pipe 14), producing 95 lbs. of sulfur by reaction with the 74 lbs. of H₂S. It may be noted at this point that counter-current flow of gas to liquor in the column 13 is important in order that, as already pointed out, the spent acid may contact the incoming H₂S so as to minimize the formation of polythionic acids or to reduce any such that are formed to sulfur. It is therefore desirable to provide the stoichiometric quantity of SO₂ to oxidize the H₂S plus what is to be desorbed by the stream of CO₂. In order to provide for 256 lbs. of SO₂ to be desorbed by the CO₂, a total quantity of 332 lbs. of SO₂ is provided in the 33,600 lbs. of water. This leaves the exiting liquor substantially free of sulfurous acid. Some polythionic acids are present in the liquor and are recirculated.

The 95 lbs. of sulfur is allowed to settle and the thickened slurry passed to the press 24. The sulfur now in the form of a still thicker slurry is conveyed to the melt tank 25a and molten sulfur is passed to the sulfur burner 26 as has already been described and addition of 60 lbs. of make-up sulfur.

672 lbs. of carbonates expressed as sodium bicarbonate is formed in the column 10 and is passed in solution in 10,000 lbs. of water to the sulfuting column 19 where it is reacted with 256 lbs. of SO₂ already mentioned, thereby producing 504 lbs. of sodium monosulfite and 352 additional pounds of CO₂ which most conveniently is vented through pipe 34.

Example 2

In this example a liquor low in sodium sulfite is used. Its composition is:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂S</td>
<td>27 lbs</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>387 lbs</td>
</tr>
<tr>
<td>Water</td>
<td>10,000 lbs</td>
</tr>
</tbody>
</table>
Upon carbonation approximately 672 lbs. of carbonates, expressed as sodium bicarbonate, is formed, together with 12 lbs. of H₂S. For oxidizing this amount of H₂S, 12 lbs. of SO₂ is consumed, leaving 256 lbs. of SO₂ for sulfiting the above quantity of carbonates as before and producing 15 lbs. of sulfur. The sulfur is recovered and burned as previously described. 119 lbs. of make-up sulfur is required, the same being admitted through pipe 27 as heretofore.

**Example 3**

In this example a smelt liquor rich in Na₂S is used which has the following composition:

| Na₂S, lbs. | 311 |
| Na₂CO₃, lbs. | 0 |
| Water, lbs. | 10,000 |

Upon carbonation, 136 lbs. of H₂S is formed in the same 2000 lbs. of CO₂, it being noted that more CO₂ is consumed because of the greater amount of H₂S formed. The carbonates formed, expressed as NaHCO₃ are approximately 672 lbs. as in the preceding examples. In order to oxidize the 136 lbs. of H₂S, 140 lbs. of SO₂ is required, sufficient additional SO₂ being dissolved to bring the SO₂ content of the discarded CO₂ to the same value of 256 lbs. as in the preceding examples. 170 lbs. of sulfur is formed which is fed to the sulfur burner 26 as before. 24 lbs. of make-up sulfur is needed in this example.

In the above examples, the temperature within the column 10 is maintained at the ordinary ambient temperatures, i.e., 40–80° F. for the region of Charleston, S. C. Elevating the temperature of the liquor during carbonation results in a shift of the equilibrium to give less bicarbonate formation. At about 160° F. a solution having a maximum of about 15% sodium monosulfide is produced. The proportion of the monocarbonate to bicarbonate is not critical provided only that the removal of the sulfide sulfur is complete. However, by thus throwing the equilibrium in the direction of the monocarbonate formation, a higher concentration of smelt liquor may be employed without precipitation of NaHCO₃ and consequently a higher concentration of sodium sulfate solution may be obtained as the final product of the system.

If desired, instead of carrying out both the operations of stripping the SO₂ from the H₂SO₃ solution and oxidizing the H₂S in the same tower, these operations may be carried out separately. Thus the gaseous mixture from the carbonator may be led to a first or oxidizing column and there contacted with a solution of H₂SO₃ in sufficient amount to oxidize the H₂S to elemental sulfur substantially quantitatively and the resulting sulfur slurry passed to a settling tank as heretofore described. The oxidation of H₂S can if desired be effected by use of gaseous SO₂ instead of H₂SO₃ as is apparent to those skilled in the art. Hence the use of the expression "SO₂" as the reagent in the oxidation of H₂S to elemental sulfur should be taken to embrace both the gaseous SO₂ and its equivalent solution form, H₂SO₃. Then the gas stream deprived of its H₂S but containing some acquired SO₂ is passed to a second or stripping column to which a further supply of H₂SO₃ is admitted and in which the required amount of SO₂ is picked up by the gaseous stream. As a result, the gas leaving the second column is passed directly to the SO₂ absorber. By so conducting the oxidizing and stripping operations in two steps instead of one, the concentration of H₂SO₃ may be varied in the two columns to suit the conditions then obtaining. Furthermore the sulfur slurry obtained in the oxidizing column will be advantageously somewhat more concentrated.

In the foregoing examples the sulfur lost has amounted to approximately 15% chiefly as polythionic acids; in larger scale operations it would be expected that such loss would be considerably less.

Also in lieu of the rather dilute solution of smelt liquor as set forth in the above, specific examples, a stronger smelt solution may be used in the initial carbonation step, i.e., one containing in the neighborhood of 20% solids. Then during the carbonation, the soluble sodium bicarbonate formed will be stripped out. At the completion of the carbonation, the precipitate of sodium bicarbonate may be filtered off and washed, thereby giving a sodium bicarbonate of high purity. The mother liquor filtered off may then be sent back to the evaporators to be added to the concentrate which is about to be burned to form a new smelt. The resulting sodium bicarbonate may then be dissolved in sufficient water and sulfitized in the manner already described.

Various modifications will occur to those skilled in the art within the spirit of the present invention. For example, if desired the carbonating column may be superimposed upon the sulfitizing column in such a manner that there will be created a lower sulfitizing zone and an upper carbonating zone and the same result had.

It will be understood that if desired the sulfitizing operation instead of being carried to the complete formation of monosulfite may be carried merely to a partially sulfitized stage consisting of a mixture of sodium sulfide, which and the sodium salts of carbonic acid, in which case a gaseous mixture weaker in SO₂ will be used.

Likewise the sulfitizing operation may be carried out to produce sodium bisulfite by the use of a gaseous mixture containing a greater portion of SO₂. Or, if desired, a product may be obtained comprising a mixture of the monosulfite and bisulfite salts. By using even greater portions of SO₂ mixtures of sodium bisulfite and free sulfuric acid can be produced. By so proceeding the process will be adapted for furnishing cooking liquor suitable for the soda base acid sulfite process provided only that the waste liquor from such process be satisfactorily concentrated and burned to produce a smelt liquor.

When wood pulp is manufactured by digesting the wood in sulfuric acid which is wholly or partially combined with an alkali metal (sodium) and the resultant black liquor collected and burned in a smelt furnace, a smelt liquor which when dissolved in water is termed a smelt liquor. Smelt liquor is frequently called green liquor because impurities are often present which impart a green color to the solution. The smelt liquor is essentially a solution of sodium sulfide and sodium carbonate. The present process provides a method whereby the smelt liquor can be converted to fresh pulping liquor. I claim:

1. The method of converting sodium sulfide, together with any sodium carbonate present in smelt liquor obtained from the pulping of wood, to sodium sulfite which comprises passing a stream of CO₂ into contact with said liquor to carbonate same with the formation of sodium salts of carbonic acid and H₂S and continuing such passage of such stream until such H₂S is stripped substantially completely from said liquor, passing the H₂S bearing stream of CO₂ to an oxidizing zone wherein said stream is brought into contact with SO₂ whereby to oxidize said H₂S to elemental sulfur, removing said sulfur from said stream, enriching said stream of CO₂ with SO₂, utilizing said SO₂ enriched stream to sulfite the already carbonated smelt liquor to continually convert the carbonates present to sulfites and to obtain substantially pure CO₂ and utilizing said CO₂ so obtained to carbonate fresh smelt liquor, the amount of CO₂ used in the carbonating step being at least five times the stoichiometric requirement.

2. The method of converting sodium sulfide, together with any sodium carbonate present in smelt liquor obtained from the pulping of wood, to sodium sulfite, which comprises passing a stream of CO₂ in intimate contact with said liquor to carbonate same with the formation of sodium sulfite of carbonic acid and H₂S and simultaneously to strip from said liquor said H₂S, the quantity
of CO₂ utilized being in substantial excess of the stoichiometric amount for carbonating said liquor to effect a substantially complete stripping of said H₂S from said liquor by CO₂ sweeping, passing the H₂S-bearing stream of CO₂ to an oxidizing zone wherein said stream is brought into contact with SO₂ whereby to oxidize said H₂S to elemental sulphur, removing said sulphur from said stream, enriching said stream of CO₂ with SO₂ and utilizing said SO₂-enriched stream to sulfite the already carbonated smelt liquor to convert the carbonates present to sulfites and to obtain substantially pure CO₂.

3. The method as defined in claim 2, wherein said stream of CO₂ is caused to be enriched with SO₂ simultaneously with said oxidizing step.

4. The method as defined in claim 2, wherein the oxidation of the H₂S is brought about by contacting the CO₂ stream bearing the same with SO₂ in aqueous solution in countercurrent manner, whereby said solution of SO₂ is substantially spent upon initial contact with said stream.

5. The method as defined in claim 2, wherein the elemental sulfur obtained and removed in the oxidation of H₂S is burned to SO₂ and such SO₂ utilized for the oxidation of H₂S and enrichment of the CO₂ stream.

6. The method as defined in claim 2, wherein the amount of SO₂ incorporated in the stream of CO₂ as a result of the enrichment step bears a substantially stoichiometric relationship to the amount of sodium salts of carbonic acid formed in the carbonating step.

7. The method of converting a solution of sodium sulfide to sodium sulfite, which comprises passing a stream of CO₂ in intimate contact with said solution to carbonate same with the formation of sodium salts of carbonic acid and H₂S and simultaneously to strip from said solution said H₂S, the quantity of CO₂ utilized being in substantial excess of the stoichiometric amount for carbonating said solution to effect a substantially complete stripping of said H₂S from said solution by CO₂ sweeping, passing the H₂S-bearing stream of CO₂ to an oxidizing zone wherein said stream is brought into contact with SO₂ whereby to oxidize said H₂S to elemental sulphur, removing said sulphur from said stream, enriching said stream of CO₂ with SO₂ and utilizing said SO₂-enriched stream to sulfite the already carbonated solution to convert the carbonates present to sulfites and to obtain substantially pure CO₂.

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