April 23, 1957 W. S. COOK 2,789,883

PROCESS FOR MONOSULFITE RECOVERY

Filed July 29, 1952 2 Sheets-Sheet 1

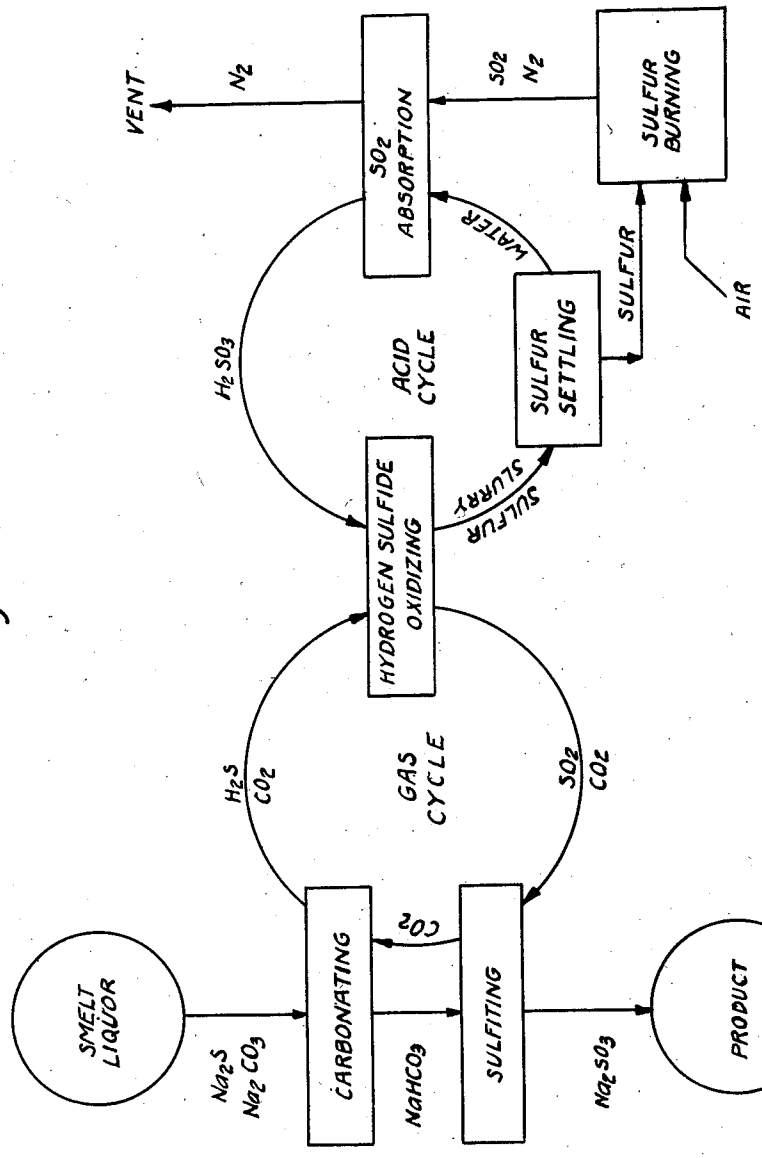

Fig. 1.

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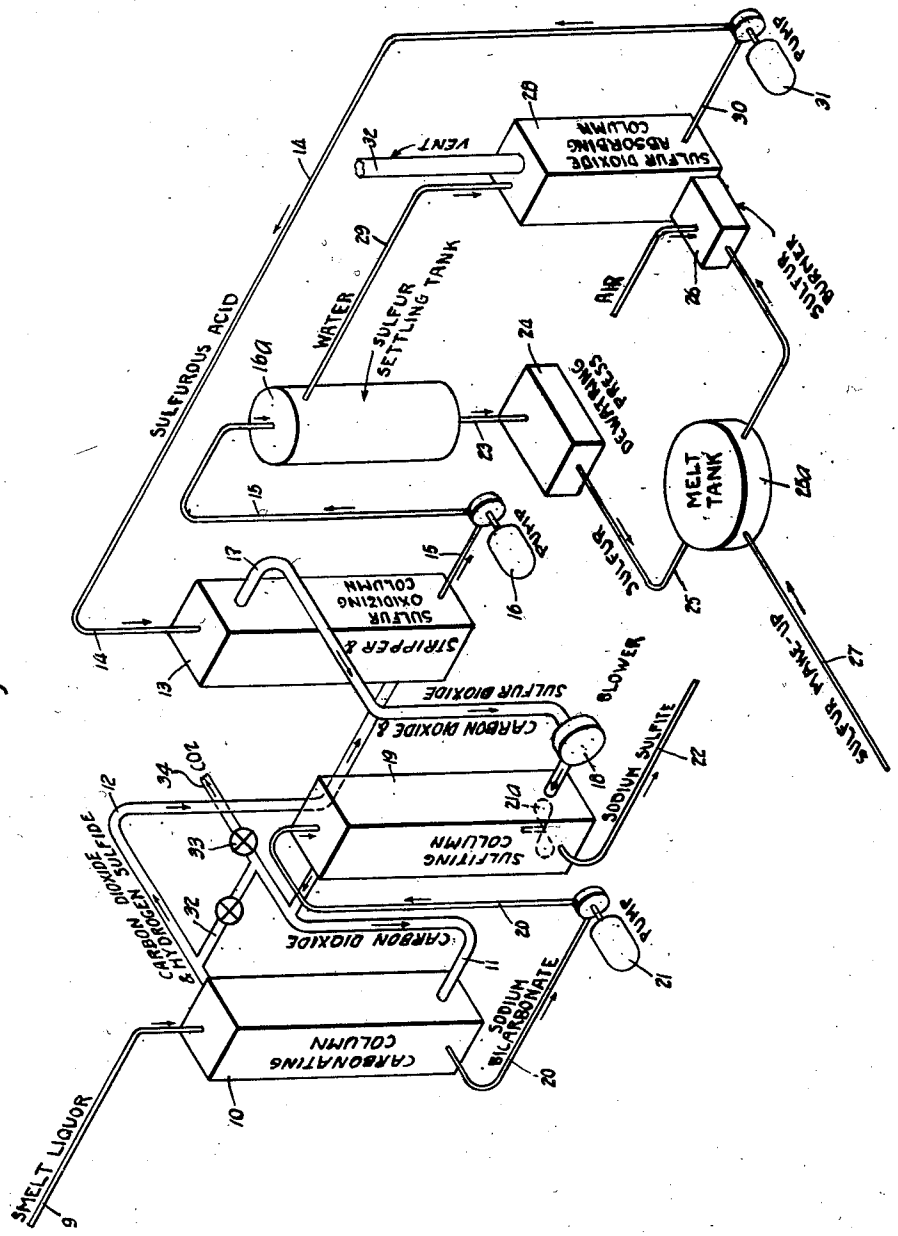

Fig. 2.

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2,789,883

PROCESS FOR MONOSULFITE RECOVERY

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Application July 29, 1952, Serial No. 301,449

7 Claims. (Cl. 23—129)

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 named 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 sulfiide 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 sulfurous 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 carbonating 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 sulfurous 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) $Na_2CO_3+CO_2(\text{in excess})+H_2O\rightarrow 2NaHCO_3$

(2) $Na_2S+CO_2(\text{in excess})+2H_2O\rightarrow 2NaHCO_3+H_2S\uparrow$

(3) $2H_2S+H_2SO_3\rightarrow 3S+3H_2O$

(4) $H_2SO_3\rightarrow H_2O+SO_2\uparrow$

(5) $2NaHCO_3+SO_2+H_2O\rightarrow Na_2SO_3+2CO_2\uparrow+2H_2O$

(6) $Na_2CO_3+SO_2+H_2O\rightarrow Na_2SO_3+CO_2\uparrow+H_2O$

(7) $S+O_2(\text{air})\rightarrow SO_2$

(8) $SO_2+H_2O\rightarrow H_2SO_3$

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 carbonating 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:

$$2Na_2S+2Na_2CO_3+4SO_2+H_2O\rightarrow 3Na_2S_2O_3+2NaHCO_3$$

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 sulfurous acid, H_2SO_3; for sodium sulfide, Na_2S; for sodium sulfite, Na_2SO_3; for so-

dium monocarbonate, Na_2CO_3; for sodium bicarbonate, $NaHCO_3$.

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** countercurrent to a stream of substantially pure CO_2 introduced at the bottom thereof through the pipe **11**. The carbonation as represented by Equations 1 and 2 takes place and the excess CO_2 sweeps with it the formed H_2S out the top of the column through pipe **12** through which it is conveyed to the bottom of column **13** which is the sulfur oxidizing column and stripper. Normally the H_2S formed will be about 10% of the mixture of CO_2 and H_2S, i. e., 7 moles of CO_2 to one mole of H_2S. There the H_2S meets the H_2SO_3 introduced into the top thereof through pipe **14** and in the column the oxidation of the H_2S to elemental sulfur (Equation 3) 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 **16***a*. By having the H_2SO_3 as nearly spent as possible at the bottom of the tower where it meets the incoming CO_2 and H_2S mixture, any polythionic acids formed further up the tower or elsewhere will be largely reduced to sulfur.

The CO_2 stream in column **13** desorbs some of the SO_2 and this mixture of CO_2 and SO_2 leaves the top of the column through pipe **17**, and aided by the blower **18** is introduced into the bottom of sulfiting 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 **21***a* in column **19** serves the purpose of releasing dissolved CO_2 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 **16***a* 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 **25***a* and thence to sulfur burner **26**. Make-up sulfur is added to tank **25***a* through pipe **27**. The products of the air oxidation of the sulfur pass through the column **28**, the SO_2 removed by the action of water from tank **16***a* introduced into the column through pipe **29**. The H_2SO_3 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 CO_2 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 CO_2 and SO_2, which is dependent on the partial pressure of SO_2 over the sulfurous acid. In this manner the CO_2 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 SO_2 is also raised so that when the SO_2 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 SO_2 to be desorbed by the CO_2 in the stripping operation. Lower temperatures are advantageous in avoiding vent losses.

The amount of SO_2 desorbed in sulfiting column **19** will bear a substantially stoichiometric relationship to the amount of sodium salts of carbonic acid formed in the carbonating step, it being noted from Equations 5 and 6 that one mole of SO_2 is needed for each two mols of sodium present regardless of the amount of the carbonic acid radical present. The excess CO_2 may if desired be carried along through the carbonator provided the column will accept so large a gas flow. Preferably a valved by-pass **32** is employed for the purpose of by-passing a portion of the CO_2. Where the amount of CO_2 increases beyond that needed as make-up for losses, as may happen through the operation of Equation 5, the excess is bled off through valved by-pass **34** to disposition not shown.

It will be noted that the concentration of the H_2SO_3 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 SO_2 in the resulting solution is such as to limit the amount of dissolved SO_2 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 SO_2 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 use 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:

Na_2S, lbs	180
Na_2CO_3, lbs	180
Water, lbs	10,000

To run this amount of liquor, 2000 lbs. of CO_2 is admitted through pipe **11**. When the reaction is complete, 74 lbs. of H_2S is formed and added to the 2000 lbs. of CO_2 leaving the top of the carbonating column through pipe **12**. 332 lbs. of SO_2 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 H_2S. 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 H_2S 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 SO_2 to oxidize the H_2S plus what is to be desorbed by the stream of CO_2. In order to provide for 256 lbs. of SO_2 to be desorbed by the CO_2, a total quantity of 332 lbs. of SO_2 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 **25***a* and molten sulfur is passed to the sulfur burner **26** as has already been described and additioned by 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 sulfiting column **19** where it is reacted with 256 lbs. of SO_2 already mentioned, thereby producing 504 lbs. of sodium monosulfite and 352 additional pounds of CO_2 which most conveniently is vented through pipe **34**.

Example 2

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

Na_2S, lbs	27
Na_2CO_3, lbs	387
Water, lbs	10,000

Upon carbonation approximately 672 lbs. of carbonates, expressed as sodium bicarbonate, is formed, together with 12 lbs. of H_2S. For oxidizing this amount of H_2S, 12 lbs. of SO_2 is consumed, leaving 256 lbs. of SO_2 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 Na_2S is used which has the following composition:

Na_2S, lbs.	311
Na_2CO_3, lbs.	0
Water, lbs.	10,000

Upon carbonation, 136 lbs. of H_2S is formed in the same 2000 lbs. of CO_2, it being noted that more CO_2 is consumed because of the greater amount of H_2S formed. The carbonates formed, expressed as $NaHCO_3$ are approximately 672 lbs. as in the preceding examples. In order to oxidize the 136 lbs. of H_2S, 140 lbs. of SO_2 is required, sufficient additional SO_2 being desorbed to bring the SO_2 content of the exiting CO_2 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 monosulfite 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 $NaHCO_3$ and consequently a higher concentration of sodium sulfite solution may be obtained as the final product of the system.

If desired, instead of carrying out both the operations of stripping the SO_2 from the H_2SO_3 solution and oxidizing the H_2S 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 H_2SO_3 in sufficient amount to oxidize the H_2S to elemental sulfur substantially quantitatively and the resulting sulfur slurry passed to a settling tank as heretofore described. The oxidation of H_2S can if desired be effected by use of gaseous SO_2 instead of H_2SO_3, as is apparent to those skilled in the art. Hence the use of the expression "SO_2" as the reagent in the oxidation of H_2S to elemental sulfur should be taken to embrace both the gaseous SO_2 and its equivalent solution form, H_2SO_3. Then the gas stream deprived of its H_2S but containing some acquired SO_2 is passed to a second or stripping column to which a further supply of H_2SO_3 is admitted and in which the required amount of SO_2 is picked up by the gaseous stream. Spent acid from the stripping column is passed directly to the SO_2 adsorber. By so conducting the oxidizing and stripping operations in two steps instead of one, the concentration of H_2SO_3 may be varied in the two columns best to suit the conditions there 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 relatively insoluble sodium bicarbonate formed will precipitate 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 recovered sodium bicarbonate may then be dissolved in sufficient water and sulfited 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 sulfiting column in such a manner that there will be created a lower sulfiting zone and an upper carbonating zone and the same result had.

It will be understood that if desired the sulfiting operation instead of being carried to the complete formation of monosulfite may be carried merely to a partially sulfited stage consisting of a mixture of sodium sulfite and the sodium salts of carbonic acid, in which case a gaseous mixture weaker in SO_2 will be used.

Likewise the sulfiting operation may be carried out to produce sodium bisulfite by the use of a gaseous mixture containing a greater portion of SO_2. Or, if desired, a product may be obtained comprising a mixture of the monosulfite and bisulfite salts. By using even greater portions of SO_2 mixtures of sodium bisulfite and free sulfurous acid can be produced. By so proceeding the process will be adatped for furnishing cooking liquod 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 sulfurous acid which is wholly or partially combined with an alkali metal (sodium) and the resultant black liquor collected and burned in a smelter furnace, a smelt results 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 CO_2 into contact with said liquor to carbonate same with the formation of sodium salts of carbonic acid and H_2S and continuing such passage of such stream until such H_2S is stripped substantially completely from said liquor, passing the H_2S bearing stream of CO_2 to an oxidizing zone wherein said stream is brought into contact with SO_2 whereby to oxidize said H_2S to elemental sulfur, removing said sulfur from said stream, enriching said stream of CO_2 with SO_2, utilizing said SO_2 enriched stream to sulfite the already carbonated smelt liquor to convert the carbonates present to sulfites and to obtain substantially pure CO_2, and utilizing said CO_2 so obtained to carbonate a fresh supply of smelt liquor, the amount of CO_2 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 CO_2 in intimate contact with said liquor to carbonate same with the formation of sodium salts of carbonic acid and H_2S and simultaneously to strip from said liquor said H_2S, the quantity

of CO_2 utilized being in substantial excess of the stoichiometric amount for carbonating said liquor to effect a substantially complete stripping of said H_2S from said liquor by CO_2 sweeping, passing the H_2S-bearing stream of CO_2 to an oxidizing zone wherein said stream is brought into contact with SO_2 whereby to oxidize said H_2S to elemental sulphur, removing said sulphur from said stream, enriching said stream of CO_2 with SO_2, and utilizing said SO_2-enriched stream to sulfite the already carbonated smelt liquor to convert the carbonates present to sulfites and to obtain substantially pure CO_2.

3. The method as defined in claim 2, wherein said stream of CO_2 is caused to be enriched with SO_2 simultaneously with said oxidizing step.

4. The method as defined in claim 2, wherein the oxidation of the H_2S is brought about by contacting the CO_2 stream bearing the same with SO_2 in aqueous solution in countercurrent manner, whereby said solution of SO_2 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 H_2S is burned to SO_2 and such SO_2 utilized for the oxidation of H_2S and enrichment of the CO_2 stream.

6. The method as defined in claim 2, wherein the amount of SO_2 incorporated in the stream of CO_2 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 CO_2 in intimate contact with said solution to carbonate same with the formation of sodium salts of carbonic acid and H_2S and simultaneously to strip from said solution said H_2S, the quantity of CO_2 utilized being in substantial excess of the stoichiometric amount for carbonating said solution to effect a substantially complete stripping of said H_2S from said solution by CO_2 sweeping, passing the H_2S-bearing stream of CO_2 to an oxidizing zone wherein said stream is brought into contact with SO_2 whereby to oxidize said H_2S to elemental sulphur, removing said sulphur from said stream, enriching said stream of CO_2 with SO_2, and utilizing said SO_2-enriched stream to sulfite the already carbonated solution to convert the carbonates present to sulfites and to obtain substantially pure CO_2.

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