

Aug. 13, 1957

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2,802,791

TREATMENT OF SPENT SULFITE LIQUOR

Filed Sept. 28, 1953

6 Sheets-Sheet 1

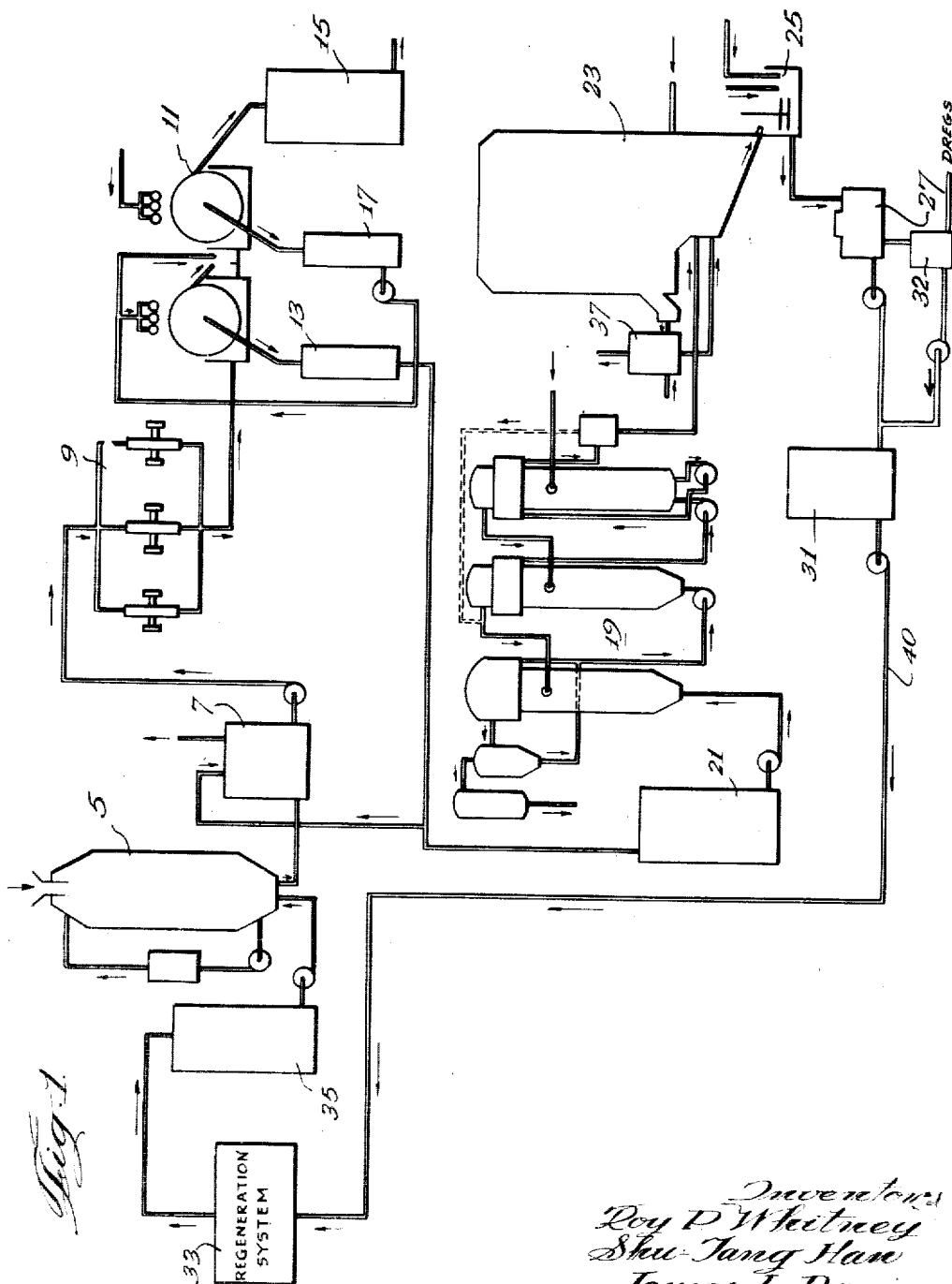


Fig. 1

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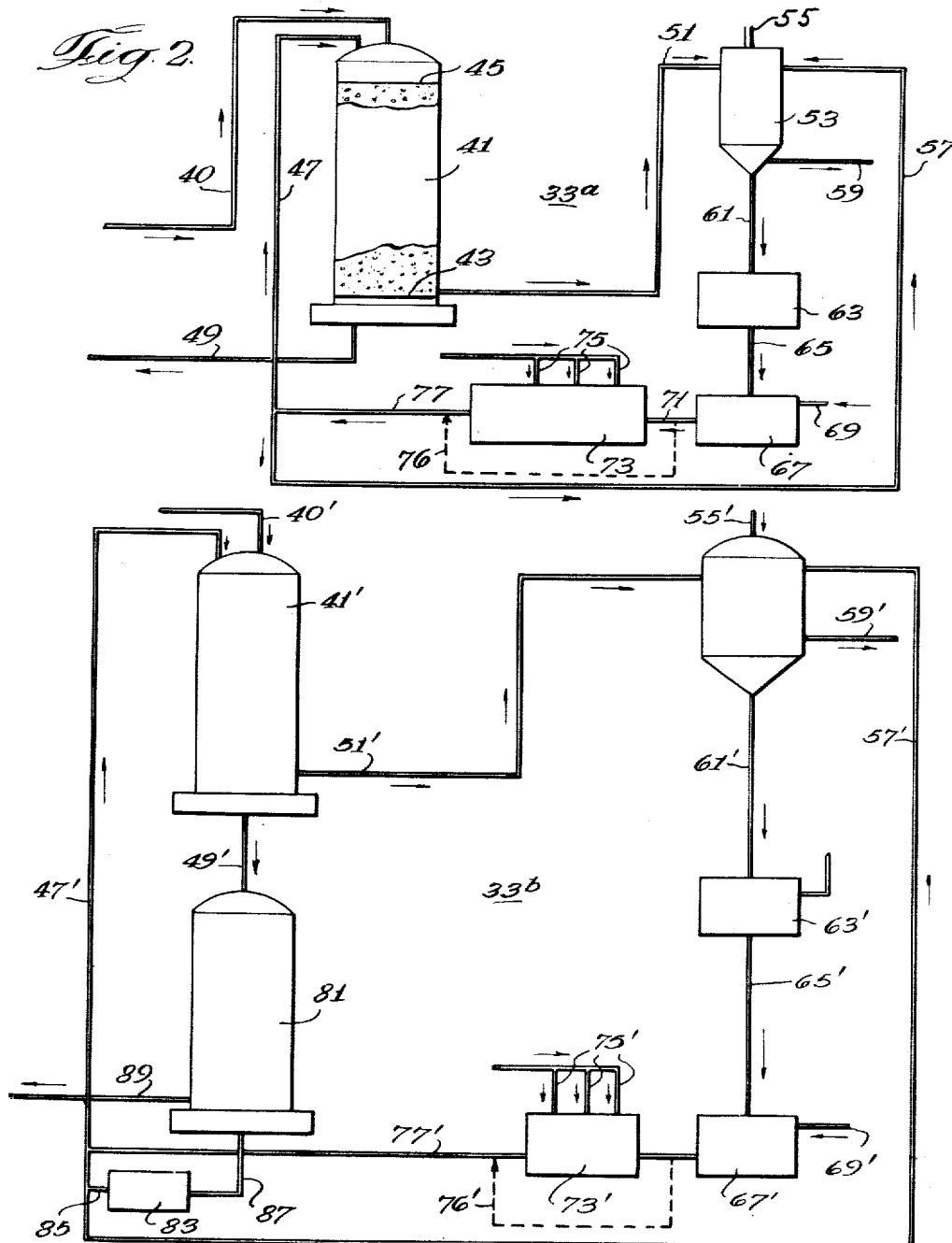
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TREATMENT OF SPENT SULFITE LIQUOR

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6 Sheets-Sheet 2



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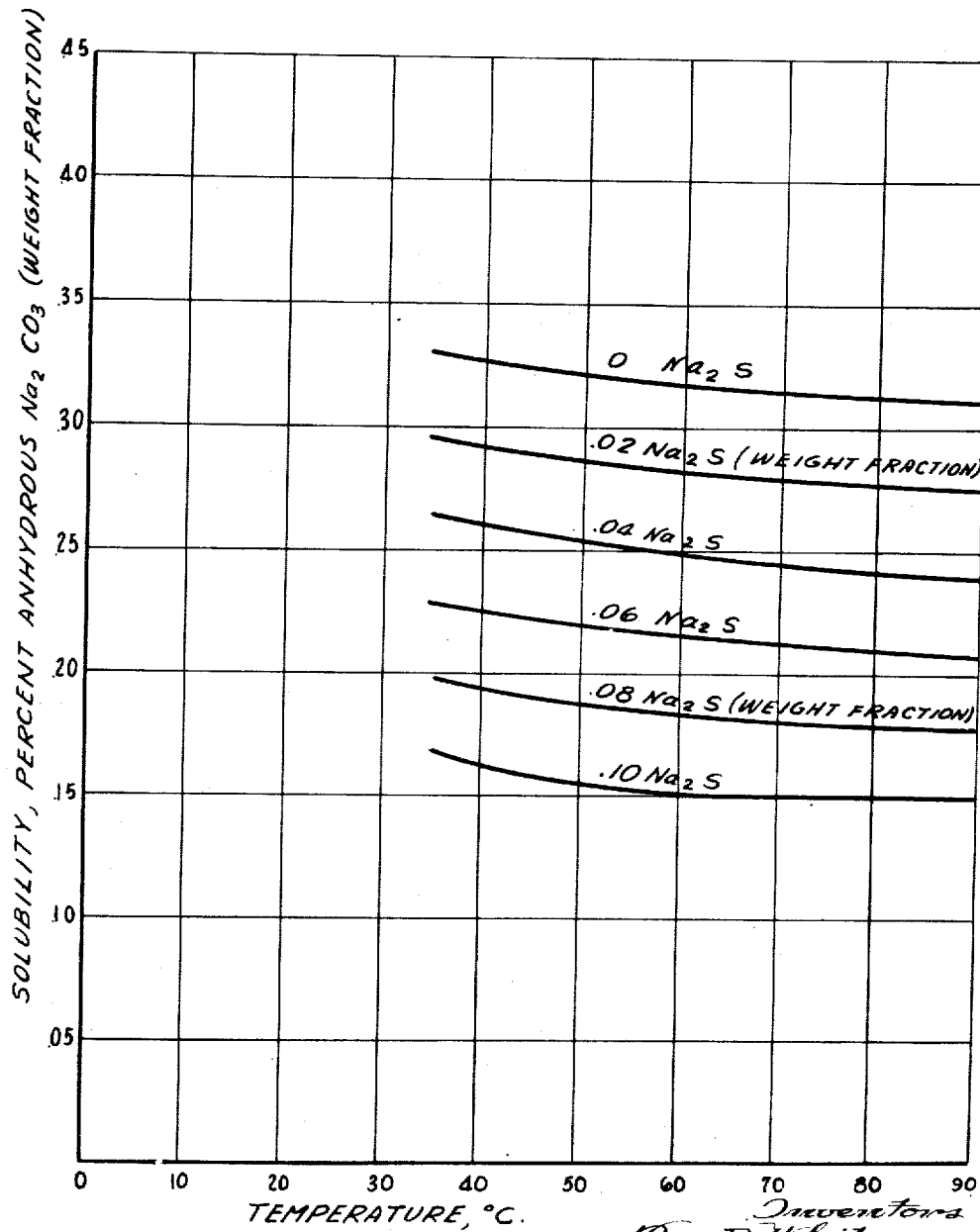
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TREATMENT OF SPENT SULFITE LIQUOR

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Fig. 4.



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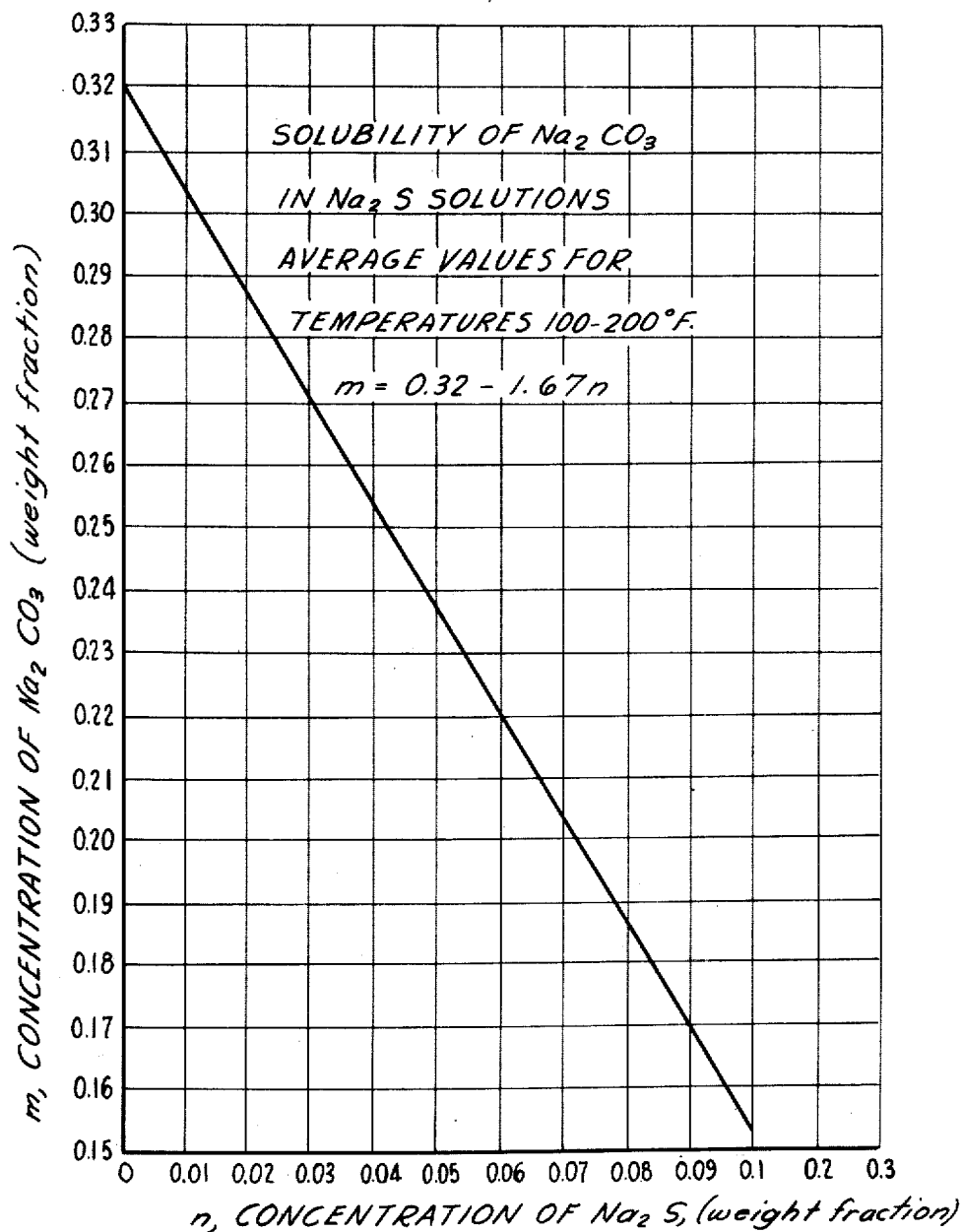
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TREATMENT OF SPENT SULFITE LIQUOR

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6 Sheets-Sheet 4

Fig. 5.



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TREATMENT OF SPENT SULFITE LIQUOR

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6 Sheets-Sheet 5

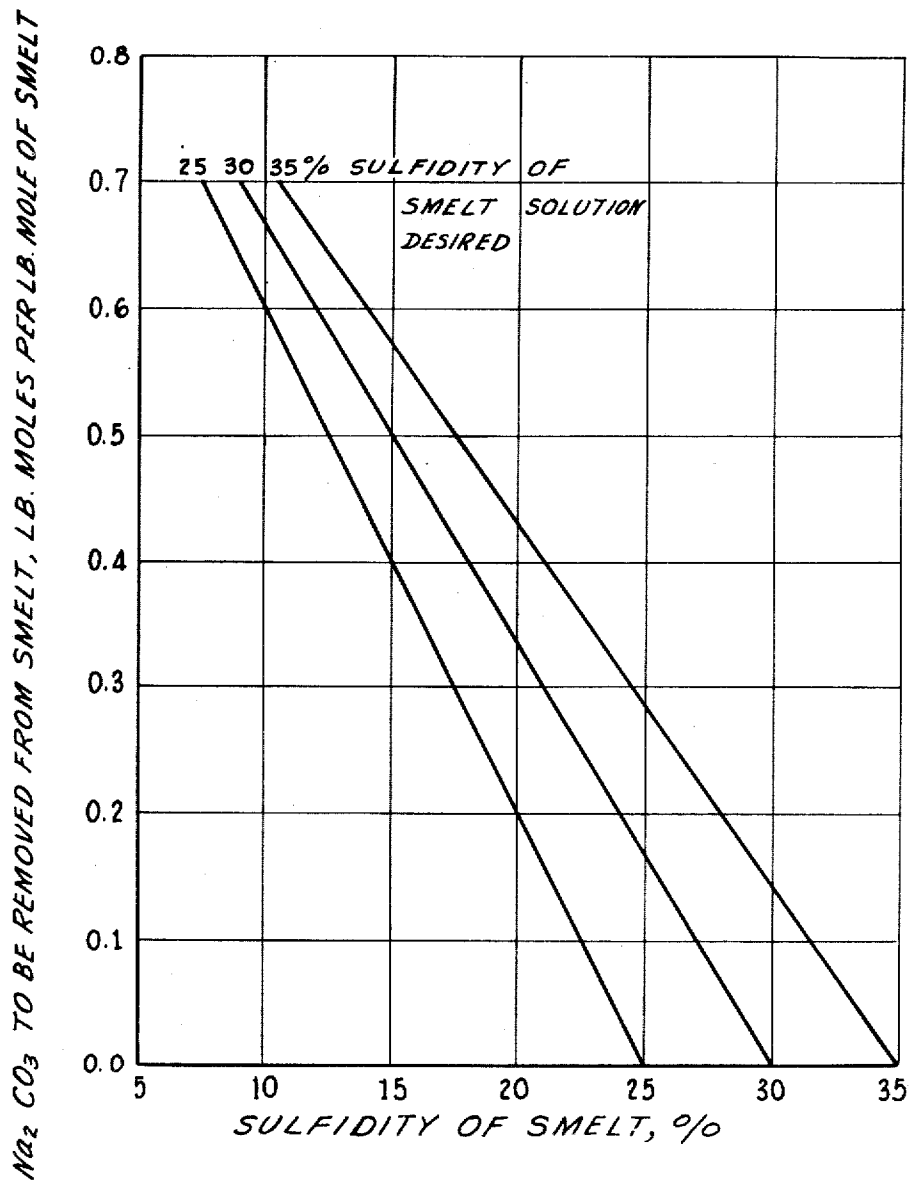


Fig. 6.

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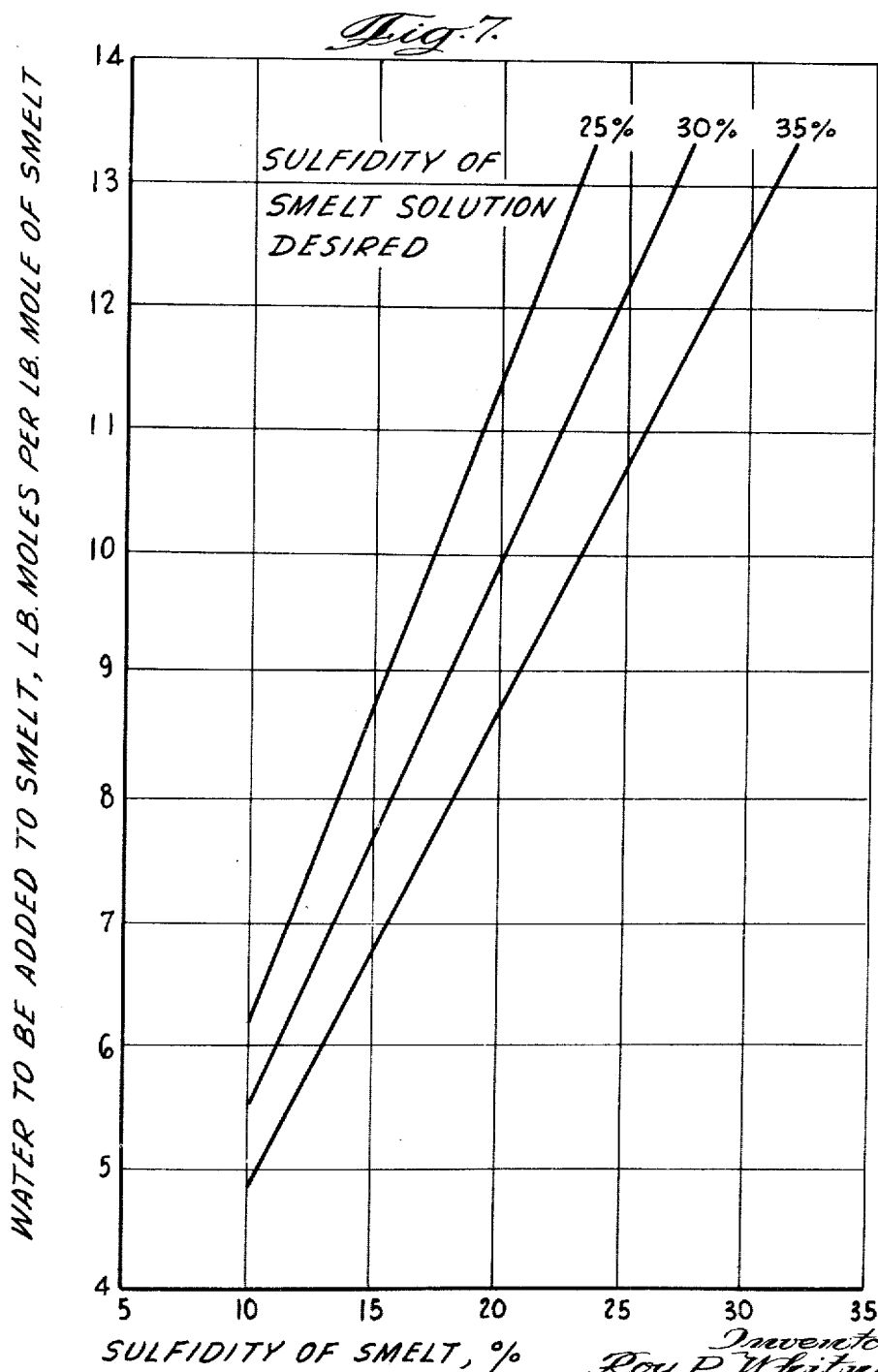
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TREATMENT OF SPENT SULFITE LIQUOR

Filed Sept. 28, 1953

6 Sheets-Sheet 6



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2,802,791

TREATMENT OF SPENT SULFITE LIQUOR

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Application September 28, 1953, Serial No. 382,678

8 Claims. (Cl. 252—183)

The present invention relates generally to the preparation of wood pulp by a sulfite process using a sodium base, and more particularly, it relates to improvements in such a process including the more efficient recovery of the cooking agents.

As is well known, most paper and paper products are manufactured from wood which has been converted into pulp. The pulp may be prepared by any of several processes including the mechanical process, and the various chemical and semichemical processes such as the acid sulfite, neutral sulfite, sulfate, and soda processes. While the mechanical and chemical processes have been widely used, it has only been in recent years that the semichemical pulping processes have achieved substantial importance despite their high yields. Such high yields are possible since, in the semichemical pulping processes, the wood is treated mildly by one of the chemical processes so that only a portion of the ligneous materials is removed from the wood.

As indicated, wood treated in accordance with a semichemical pulping process may be digested in substantially the same manner as in any one of the chemical processes, such as the sulfite and sulfate processes, but the neutral sulfite process is preferred, in many cases, because of the potential economies of the process and the properties of the resulting pulp.

However, there has been a serious limitation upon the use of the neutral sulfite semichemical pulping process in that the materials employed in treating the wood, including a sodium base, have not been economically recoverable. As a result, the process has been relatively expensive, and the use of this semichemical pulping process has been limited. Various attempts to provide simple recovery processes, to reduce the cost of the recovery processes and to successfully regenerate the spent liquor have not solved the problem even though the solution of the problem has been sought for years.

In view of the failure to solve the problem of economically recovering the cooking agents used in the neutral sulfite semichemical pulping process and regenerating the spent liquor, the use of such process has been substantially limited to those paper mills which can afford to lose the liquor or which can operate on what is known as a cross-recovery system. In the latter case, the spent liquor of the semichemical pulping process is not regenerated for the semichemical pulping process, but the process is used in conjunction with the well-known sulfate or kraft process and the spent neutral sulfite liquor of the semichemical pulping process is used as a make-up in the recovery system of the kraft process. The use of the cross-recovery system imposes a substantial restriction on the relative production of the semichemical pulping process so that the process, in the past, has only been used in a small way and the output of neutral sulfite semichemical pulp has been limited.

In the neutral sulfite semichemical pulping process, sodium sulfite in aqueous solution is primarily used in the cooking agent employed for cooking or digesting the

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wood to make the pulp. Smaller amounts of sodium hydroxide, sodium carbonate, or sodium bicarbonate are also used in making up the cooking agent. The conditions used in the original cooking are considerably less severe than those employed in the more common chemical processes, and as pointed out, less ligneous materials are removed so that the substantially higher yields are obtained in the semichemical process than in any of the aforementioned chemical processes.

The pulp produced by the neutral sulfite semichemical pulping process possesses strength and bleachability characteristics which are intermediate to the characteristics of the more common kraft and acid sulfite pulps. These and other characteristics have made the neutral sulfite semichemical pulp very useful in the manufacture of paper and paperboard, such as corrugating medium, test liners, specialty board and, to some extent, wall board and insulating paper or board. Furthermore, the semichemical pulp is bleached and combined with other pulps for making high grade paper such as book paper and for making glassine.

Despite the many uses of the pulp, the use of the sulfite semichemical pulping process, as above indicated, has been restricted primarily because of the lack of an economical method for recovering the cooking agent from the spent sodium base neutral sulfite liquor. In this connection, no commercially successful process has been developed for independently recovering the cooking agent and regenerating the spent sulfite liquor. Attempts have been made to regenerate the spent liquor by first treating it in a manner similar to the direct recovery method employed in the kraft process, that is, by concentrating the waste liquor, burning the concentrate to provide a smelt, and dissolving the smelt to provide an aqueous solution; and then treating the aqueous solution of the resulting smelt with sulfur dioxide. However, this has, in the past, resulted in the excessive formation of thiosulfates and other polythionic compounds whose presence is not wanted in the digestion of wood.

Attempts have also been made to oxidize a material prepared from the smelt, but these attempts have likewise been unsuccessful for commercial use. Similarly, carbonation processes for recovering the liquor have been generally discarded, largely because of their cost.

In view of the failure of the attempts to regenerate the spent liquor from the neutral sulfite semichemical pulping process, some pulp treating plants make use of the cross-recovery system mentioned above. This type of operation, as before indicated, imposes restrictions on the production of the neutral sulfite semichemical pulp mills and depends upon the operation of a conjunctive kraft production. The relative capacities of kraft and neutral sulfite mills under a joint operation depend upon the relative efficiencies of chemical recovery in the two processes and are generally considered to be limited to a ratio of about 4 to 1. This factor seriously limits the application of cross-recovery where a larger neutral sulfite production is desired.

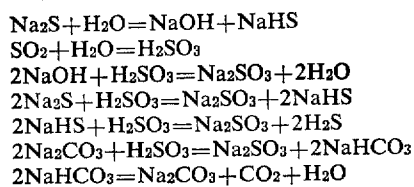
An object of the present invention is to provide a simple, economical and commercially feasible method for handling the spent liquors from the sodium base neutral sulfite semichemical pulping process. As will become more clear hereinafter, this and other objects of the invention are accomplished through a direct recovery method where spent liquors are regenerated through direct sulfitation without the production of sodium thiosulfate and other polythionic compounds to any significant degree.

In the direct recovery method of the invention, the spent sulfite liquor, which normally contains around 11 percent solids, is concentrated for burning to a solids content of between about 55 percent and about 70

percent, whereupon it is burned to form a smelt primarily comprising sodium sulfide and sodium carbonate. This smelt is dissolved to form a dilute aqueous solution containing the sodium sulfide and sodium carbonate. As indicated, previous attempts to convert the sodium sulfide for effective use in the manufacture of neutral sulfite semichemical pulp have resulted in the formation of substantial amounts of unwanted sodium thiosulfate and polythionic compounds. We have discovered, however, that under certain particular conditions, the sodium sulfide may be economically converted to sodium sulfite which can be immediately used as a cooking agent in the manufacture of semichemical pulp. This conversion is effected by direct sulfitation through treatment of the aqueous solution with sulfur dioxide gas in a manner such that formation of sodium thiosulfate and polythionates is minimized.

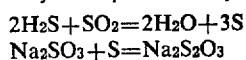
In order that the particular conditions required for converting the sodium sulfide substantially completely to sodium sulfite may be more easily understood, the mechanism of the conversion may be explained on the basis that the reaction essentially comprises a neutralization of hydrolized dibasic salts present in the aqueous solution prepared from the smelt and proceeds in what may be considered to be distinct stages.

In the first stage, sodium hydroxide resulting from the hydrolysis of sodium sulfide in the smelt reacts with sulfurous acid, resulting from the solution of sulfur dioxide in water, thereby forming sodium sulfite; and sodium sulfide which is unhydrolized is converted to sodium hydrosulfide. In the second stage, the sodium hydrosulfide of the first stage is further converted to hydrogen sulfide with the formation of more sodium sulfite through reactions with sulfurous acid which is formed through solution of sulfur dioxide, as before pointed out. The sodium carbonate present also reacts with sulfurous acid in a manner similar to the sodium sulfide to form sodium sulfite and sodium bicarbonate. Also as part of the second stage, the sodium bicarbonate may form sodium carbonate, water and carbon dioxide gas. These reactions may be represented by the following equations:



The first stage reactions proceed at a pH of about 10 or above while the second stage reactions proceed at pH values between about 8.0 and 10.0. Since the direct sulfitation process of the invention should not be carried out at pH values below about 7.0 until after substantially complete conversion of sodium sulfide and removal of hydrogen sulfide, reactions which occur at such lower pH values are discussed hereinafter. In fact, if the process is carried out to such lower pH values in the presence of hydrogen sulfide, the undesirable thiosulfates and polythionates tend to form.

It will be seen that in the second stage reactions hydrogen sulfide is formed and the presence of hydrogen sulfide becomes an important factor, resulting in secondary reactions which interfere with the production of sodium sulfite causing the formation of the unwanted compounds. For example, the hydrogen sulfide reacts with sulfur dioxide in aqueous phase to form water and colloidal sulfur. The sulfur thus formed is in a reactive state and reacts readily with sodium sulfite to form the undesired sodium thiosulfate. The mechanism of this reaction may be represented by the following two equations:



This reaction apparently proceeds in this manner contrary to the common belief that the formation of sodium thiosulfate in direct sulfitation results from the direct reaction of sodium sulfide and sulfur dioxide and is, therefore, almost unpreventable. We have now found, contrary to the teachings of the art, that the formation of the thiosulfate is dependent upon the initial reaction by the hydrogen sulfide and sulfur dioxide, and we have also found that sulfur dioxide will not react with sodium sulfide or with the hydrosulfide. Furthermore, it appears that sulfur dioxide and hydrogen sulfide do not react readily in the gaseous phase under the conditions of the invention but that they do react readily in the aqueous phase to give the undesired polythionates.

By operating under the particular conditions of the invention, the amount of thiosulfate produced can be so substantially minimized that the thiosulfate content in the regenerated liquor is no longer harmful. This minimization apparently results from inhibition of the reaction between the hydrogen sulfide with sulfur dioxide, which reaction, as pointed out, has not been believed to have controlled the thiosulfate formation. In any event, we have found that one of the conditions of our process is the avoidance of prolonged association of the aqueous solution containing hydrogen sulfide with the sulfur dioxide during sulfitation.

We have found that such condition can be most satisfactorily maintained through causing the aqueous solution and the sulfur dioxide to flow in concurrent flow under controlled conditions. Thus, prolonged association of sulfur dioxide with hydrogen sulfide may be minimized and, in the latter stages of regeneration of the liquor where the hydrogen sulfide concentration is highest, the gas is lean in sulfur dioxide.

While it is of great importance that the association of hydrogen sulfide with sulfur dioxide be minimized to prevent significant formation of sodium thiosulfate, other conditions should be established to further minimize such thiosulfate formation. One such condition that should be maintained during direct sulfitation is a relatively high temperature, and, in this connection, formation of the thiosulfates and unwanted compounds is minimized by carrying out the sulfitation at temperatures between about 60° C. and 100° C. At lower temperatures, thiosulfate formation is substantially increased while higher temperature operation is not practical.

Another condition which should be maintained is a low concentration of sulfur dioxide in the treating gas for the aqueous smelt solution and, of course, the diluting gases in the treating gas should be inert, such as nitrogen and water vapor. As a matter of practical operation, the amount of diluting gases is substantially fixed because economical manufacture of such gas determines, in large part, the percentage of sulfur dioxide. This limitation on the treating gas can, in part, be compensated for by suitable adjustment of other factors such as liquor flow rate and concentration of sodium sulfide.

Not only is it important that the association between the sulfur dioxide and hydrogen sulfide be minimized, that the concentration of sulfur dioxide be relatively low in the treating gas, and that the concentration and quantity of the sulfur dioxide be adjusted properly, but it is also quite important that the aqueous solution be uniformly contacted by the treating gas to prevent any localized acceleration of the reaction. Such uniformity of contact is promoted through the use of sulfur dioxide in gaseous form and consequently the treating gas is used in place of sulfurous acid or various bisulfite solutions. More uniformity of contact between sulfur dioxide and the aqueous solution prepared from the smelt is made possible by filming the solution, as in a packed tower.

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In addition to the foregoing conditions which are important in the regeneration of spent sulfite liquor, the aqueous solution made from the smelt should be dilute. In this connection, the sodium sulfide content of the aqueous solution should not exceed about 1.2 moles per liter.

A further description of the present invention will be made in connection with the attached sheets of drawings which illustrate various ways of practicing the principles of the present invention.

Figure 1 is an overall flow diagram illustrating a process for preparing pulp by a semichemical pulping process wherein the spent liquor is regenerated and used in the pulp preparation;

Figure 2 is a flow diagram particularly illustrating the portion of the process directed to the regeneration of spent neutral sulfite liquor;

Figure 3 is also a flow diagram illustrating a modified form of the invention in which the portion of the system illustrated is adapted for regenerating spent acid sulfite liquor;

Figure 4 is a graph showing the solubility of sodium carbonate in solutions containing different amounts of sodium sulfide at temperatures from about 100° F. to 200° F.;

Figure 5 is a graph illustrating the relationship between the weight fractions of sodium carbonate and sodium sulfide at temperatures between about 100° F. and about 200° F., average values being plotted from the graph shown in Figure 4;

Figure 6 is another graph showing the relationship between the sulfidity of the smelt, the sulfidity of the smelt solution, and the amount of sodium carbonate to be removed from the smelt in pound-moles per pound-mole of smelt; and

Figure 7 is still another graph from which can be computed the amount of water to be added, in pound-moles per pound-mole of smelt, to a given smelt to provide a solution of desired sulfidity.

The invention is particularly directed to the sulfite, semichemical pulping process using a sodium base and, in accordance with this process and, as shown in Figure 1, wood chips are introduced into a digester 5 and treated with sulfite liquor in accordance with the semichemical pulping process so that only a portion of the ligneous materials is removed. The contents of the digester are discharged into a bowl tank 7 and pumped to refiners 9 wherein the chips are mechanically defibered. From the refiners 9, the pulp and spent liquor from the digester are conducted to vacuum washers 11 in which the spent liquor is separated from the pulp. The spent liquor is discharged into a storage tank 13 and the pulp conveyed to a stock chest 15 for use in making paper and paper products. The washers 11 may be connected in series, as illustrated, and in such an arrangement, the wash liquor from the later washers is used in the earlier washers. In the series arrangement, the wash liquor is stored in a tank 17 and pumped to an earlier washer. The digestion, refining, and washing steps described are well known and do not comprise a part of our invention.

The spent sulfite liquor, which is to be regenerated in accordance with the invention, is then concentrated in evaporators 19, the liquor being conducted from the storage tank 13 to an evaporator feed tank 21 for pumping into the evaporators. The concentrated liquor is burned in a furnace 23 to produce a smelt primarily comprising sodium sulfide and sodium carbonate. The smelt is dissolved in a tank 25 to provide the dilute aqueous solution and passed to a clarifier 27. After

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clarification, the aqueous solution may be pumped to a tank 31, the dregs from the clarifier 27 being washed in a dregs washer 32.

The aqueous solution is then pumped to a regeneration system 33 in which the aqueous solution is converted to treating liquor and stored in a tank 35 for use in the digester 5. The regeneration system may be of the type shown in Figure 2 if a neutral sulfite process is used but may be of the type shown in Figure 3 if an acid sulfite process is used.

The evaporators 19 and combustion furnace 23 are of conventional construction and may be of the type used in connection with the recovery system in the kraft process.

The cooking liquor for the digester 5 may vary somewhat in formula but a typical neutral sulfite liquor is set forth below, the formula below being based upon one ton of pulp produced (dry basis):

Compound	Lbs.	Lb. Mole/ 1,000 lbs. H ₂ O
Na ₂ SO ₃	340	.332
Na ₂ CO ₃	24	.028
NaHCO ₃	51	.075
Na ₂ S ₂ O ₃	41	.032
Na ₂ SO ₄	14	.012
Total.....	470	.479
H ₂ O.....	8,100	

During cooking in the digester 5, the liquor to wood ratio is maintained at a value of about 4 to 1, and the yield of semichemical pulp is normally approximately 70 percent of the wood (dry basis) introduced into the digester 5.

After the removal of the pulp from the liquor in the washers 11, the spent liquor goes into the storage tank 13 at a solids content of about 11 percent. The spent liquor may be concentrated in the evaporators 19 to produce a combustible concentrate containing about 65 percent solids and the concentrate is passed into the combustion furnace 23 and burned. The residual heat contained in the gases leaving the combustion furnace may be employed to preheat the air entering the furnace in an air preheater 37. The stack gas is vented from the air preheater 37. It will be understood that other concentration means and arrangements may be employed and that the arrangement shown is but one example of means for concentrating spent liquor.

The smelt, as indicated, is discharged from the combustion furnace 23 into the tank 25 and dissolved in water. An analysis of a typical smelt solution of the invention leaving the dissolving tank 25, on the basis of one ton of pulp, is given below:

Compound	Lbs.	Lb. Mole/ 1,000 lbs. H ₂ O
Na ₂ S.....	147	.232
NaHS.....	30	.066
NaOH.....	22	.066
Na ₂ CO ₃	114	.132
Na ₂ SO ₄	14	.012
Total.....	327	.508
H ₂ O.....	8,112	

The aqueous smelt solution is then introduced into the clarifier 27 and is ready to be subjected to the regeneration system of the invention.

In order to effect most satisfactory regeneration of the liquor, the pH of the aqueous smelt solution should be above about 11.0, the pH being preferably about 12. Adjustment of pH may be effected by addition of chemicals in the dissolving tank 25 or in the combustion furnace, if desired.

As before indicated, the regeneration system may be of two types, one type being adapted to regenerate liquor for a neutral sulfite semichemical pulping process and such a system is shown in Figure 2, this system being generally designated by numeral 33a; and the other type of system being adapted to regenerate liquor for an acid sulfite chemical pulping process and such a system is shown in Figure 3, this system being generally designated by numeral 33b.

In regeneration system 33a which provides liquor for the neutral sulfite semichemical pulp process, the aqueous smelt solution is pumped from the solution storage tank 31 (Figure 1) through a pipe 40 to the top of a packed tower 41 which may be packed with any of several commercially available packing materials such as partition rings, spiral tiles, Raschig rings, Berl saddles, wire-mesh packings, or other type of packing. The tower 41 is constructed in a manner such that the desired conditions may be maintained and, in this connection, the tower 41 is provided with a separating device 43 in the bottom to avoid unnecessary gas-liquid contact beyond the point of the desired conversion and is also provided with a gas-liquor distributor 45 in the top of the tower to insure a uniform distribution. The contacting section of the tower is insulated to minimize heat losses.

In the tower 41, the smelt solution is contacted with a concurrently flowing gaseous stream containing sulfur dioxide to convert the sodium sulfide to sulfite, the gaseous stream being introduced into the tower 41 by means of a line 47.

The gaseous stream of sulfur dioxide is preferably saturated with water vapor in order that the conversion will proceed without supplying heat to the tower. Under such saturated conditions, the conversion reaction is exothermic and with the sensible heat of the gas and aqueous solution, additional heat is not required. However, if saturated gas is not employed, heat must be employed to effect the desired conversion, the heat being supplied externally or in the form of sensible heat in the gas.

The rate of flow of the gas stream in the tower, as pointed out, is so adjusted that the sulfur dioxide in the treating gas is nearly exhausted when the sodium sulfide in the liquor is substantially converted to prevent formation of the unwanted thiosulfates. Thus, as the solution flows down through the tower, the sulfur dioxide is utilized and hydrogen sulfide is formed but at the point where substantial amounts of hydrogen sulfide are formed in the tower, the sulfur dioxide is almost completely depleted thereby minimizing formation of thiosulfates. In this connection, at the point in the tower where the pH of the aqueous solution reaches about 9.0 at least about 90 percent of the sulfur dioxide should be utilized to provide most satisfactory operation.

The liquor leaves the conversion tower 41 through a line 49 and consists primarily of a mixture of sodium sulfite, sodium bicarbonate and some sodium carbonate which is immediately ready for use in the digester 5. In order to limit substantial thiosulfate formation, the pH of the tower effluent should be above 8.5 but, in order to effect the desired conversion of the sulfide the pH should be less than 9.5.

All or a portion of the tower effluent may be added to the incoming liquor in order to raise the concentration of the sodium sulfite in the effluent. If this is done, care should be taken to assure that all of the hydrogen sulfide

has been stripped from the tower effluent prior to addition to the incoming liquor. This may be done by subjecting the effluent to vacuum conditions, steam stripping, etc. As will be recalled, any amount of hydrogen sulfide in the incoming liquor is highly susceptible to thiosulfate formation.

The gases leaving the tower 41 consist primarily of a mixture of hydrogen sulfide, carbon dioxide, nitrogen, and water vapor, and are withdrawn through a line 51, whereupon they are introduced into a hydrogen sulfide recovery tower 53. In the recovery tower, the gases may be contacted with water spray introduced through a line 55 and also with a gaseous stream containing sulfur dioxide gas introduced through a line 57.

Undissolved and unreacted exhaust gases which are discharged from the tower 53, such as nitrogen and carbon dioxide, are vented from the recovery tower 53 through a line 59, while the sulfur produced is withdrawn through a line 61, separated from the water, and collected in a melting tank 63 where the sulfur is heated to a melting temperature. Various types of recovery systems may be used in addition to that shown, and the illustrated system for recovery of hydrogen sulfide is merely illustrative.

As will be apparent from the foregoing, sulfur dioxide gas is required in the regeneration system 33a for two principal purposes, one being to convert the sodium sulfide in the conversion tower 41 by direct sulfitation and the other being to recover the sulfur from the hydrogen sulfide exhausted from the conversion tower 41, this being accomplished in the recovery tower 53 or other recovery system. Accordingly, the recovery system includes apparatus for producing treating gas containing the desired amount of sulfur dioxide gas. The treating gas is manufactured by burning sulfur from the melting tank 63 which contains sulfur from the recovery tower 53 and also sulfur which must be added to make up for losses in the system 33a.

In the illustrated system, molten sulfur is withdrawn from the tank 63 through a line 65 and is then introduced into a sulfur burner 67 which is preferably of the spray or rotary type. A controlled supply of air is also introduced into the burner 67 through a line 69. Sufficient air should be used to provide a gas having a sulfur dioxide content between about 16 and 19 percent by volume. If lesser amounts of air are employed, the sulfur tends to sublime while if larger amounts are used, the sulfur oxidizes to sulfur trioxide.

In order to provide a treating gas containing the desired amount of sulfur dioxide gas for the conversion tower 41, an amount of inert gas, such as nitrogen, may be introduced into the gas from the sulfur burner 67 so as to provide a treating gas having a ratio of inert gas to sulfur dioxide within the range of between 5 to 1, and 20 to 1.

The gaseous stream leaves the sulfur burner 67 through a line 71 and is thereupon introduced into a water saturator 73 where a plurality of lines 75 introduce water into the stream in sufficient amounts to bring the temperature of the gaseous stream to a value within the range of about 60° C. to 100° C. and preferably at the upper end of the range. As has been pointed out, saturation of the sulfur dioxide gas is preferred to effect the desired conversion. However, if the tower is heated externally or there is sufficient sensible heat in the gas, the saturator may be eliminated and, for this purpose, by-pass line 76 (shown dotted) may be provided.

The treating gas leaves the saturator 73 through a line 77 and is supplied to line 47 which feeds the gas into the conversion tower 41 concurrently with the aqueous smelt solution. The treating gas is also introduced into the recovery tower 53 through the line 57.

Typical compositions of the various gas streams are indicated in the following table:

**Compositions of gas streams on the basis of one ton
of pulp**

Constituent	Saturated Burner Gas 178° F. (81° C.)		Conversion Tower Exit Gas 178° F. (81° C.)		Recovery Tower Exhaust Gas 173° F. (78° C.)		Combustion Furnace Flue Gas 400° F. (205° C.)	
	lb. mole	Per- cent (dry basis)	lb. mole	Per- cent (dry basis)	lb. mole	Per- cent (dry basis)	lb. mole	Per- cent (dry basis)
SO ₂	268	18.0	---	---	7	0.5	31	0.2
H ₂ S.....	---	---	76	13.8	7	1.1	---	---
CO ₂	---	---	3	0.4	3	0.3	1,655	19.4
O ₂	22	3.0	16	8.1	22	3.0	128	2.0
N ₂	514	79.0	376	82.7	514	95.1	4,250	78.4
H ₂ O.....	400	---	280	---	270	---	1,228	---
Total.....	1,204	100	751	100	823	100	7,315	100

¹ Containing 24 pounds of suspended sodium sulfate not shown.

It was before pointed out that the pH of the aqueous smelt solution is important and may be adjusted so that most satisfactory conversion of the solution can be effected in the tower 41. Such pH adjustment, if necessary, decreases evolution of hydrogen sulfide in the tower and causes the hydrogen and sulfide to be retained in the solution as hydrosulfide ions. Thus, the hydrogen sulfide is not present at the top of the tower or at the earlier intermediate stages in the tower. However, in the conversion tower 41, the pH of the solution is lowered, i. e. the solution becomes less basic, and in the later stages of the conversion, where the sulfur dioxide is substantially depleted, the hydrogen sulfide dissociates to provide a liquor of the desired formula. The initial pH is, therefore, controlled to prevent evolution of hydrogen sulfide in the initial conversion stages and to permit dissociation in the late stages of conversion in the tower 41. It is necessary to allow the solution to become sufficiently less basic to permit the sodium carbonate to go to sodium bicarbonate, which conversion is substantially complete at a pH of about 9.0. Through such control, formation of unwanted compounds is inhibited and a liquor ready for use in the digester 5 is provided.

It was also previously noted that sulfur losses could be made up by sulfur addition to the melting tank 63. Sodium losses may be made up in connection with pH adjustment by addition of sodium compounds to the dissolving tank 25 or combustion chamber 23, as before indicated. However, sodium losses may be made up at still other points in the regeneration system 33a or by addition to the liquor storage tank 35. Thus, the described process is easily adaptable for making up losses and this provides a substantial advantage.

The regeneration system 33a described above is adapted for use in connection with regeneration of neutral sulfite, sodium base spent liquor but the system 33b provides liquor for an acid sulfite process, and such system is shown in Figure 3. Since the system shown in Figure 3 is substantially the same as that shown in Figure 2, corresponding units will be similarly numbered but will be differentiated by the symbol prime (').

The system 33b shown in Figure 3 for providing liquor for an acid sulphite pulping process is like that shown in Figure 2 up to the point where the liquor leaves the conversion tower 41'. At this point the liquor is basic, as above described.

The differences between the two systems 33a and 33b arise in the treatment of the liquor leaving the conversion tower 41'. For producing an acid sulfite liquor, the aqueous liquor leaving the tower 41' through the line 49', and consisting essentially of sodium sulfite and sodium bicarbonate, is introduced into an absorption tower 81 where the liquor absorbs additional amounts of sulfur dioxide. It will be noted that the liquor leaving the tower 41' has been so treated as to convert substantially all of the sodium sulfide and the conversion product hydrogen

sulfide has been removed so that further sulfiting and acidification may be practiced without formation of unwanted compounds.

As seen in Figure 3, this is done by passing the liquor from conversion tower 41' into countercurrent flow with a stream of sulfur dioxide gas. In this connection, a portion of the treating gas containing sulfur dioxide, leaving the water saturator 73' through the line 77' is conducted into a cooler 83 through pipe 85 and then into the base of the absorption tower 81 through pipe 87. Thus, in the tower 81, the liquor absorbs additional amounts of sulfur dioxide by countercurrent contact with the liquor, resulting in the production of a regenerated acid sulfite liquor containing sodium bisulfite and free sulfur dioxide. This regenerated liquor is withdrawn from the tower 81 through a line 89 for storage or immediate use in the digester 5.

In the foregoing, we have described processes for regenerating spent liquors from neutral sulfite and acid sulfite processes, which processes may be easily and economically carried out. As a result, we have provided for a long felt need in the paper industry and have provided a regeneration process which is independent of other processes.

It will be evident that various modifications can be made to the processes described without departing from the scope of the present invention. For example, the packed conversion towers 41 and 41' may be replaced by a spray tower or other type of treating chamber provided that the liquor and the gaseous stream are introduced concurrently to avoid prolonged contact between the hydrogen sulfide and the sulfur dioxide. Furthermore, since various of the conditions are interrelated, variations of these conditions to limit contact between the hydrogen sulfide and sulfur dioxide are within the scope of this invention.

The present invention is not only directed to the recovery of the spent liquor directly from a neutral sulfite mill or an acid sulfite mill but it, in addition, is also directed to improving the ratio of production of the neutral sulfite mill when used in conjunction with a kraft mill. In the latter connection, the ratio of production of a neutral sulfite mill to that of a kraft mill is about 1 to 4, as has been pointed out above. Such ratio is controlled by the amount of sodium provided by the spent liquor from the neutral sulfite process for the purpose of making up the sodium loss in the kraft process.

In accordance with the principles of the present invention, this ratio of production can be so improved that the ratio of production of the neutral sulfite mill to that of a conjunctive kraft mill can be raised from 1 to 4 to 2.8 to 4, or an increase of almost 300 percent. This is accomplished through sulfitation of a sodium carbonate solution, part of which is obtained from the kraft recovery process. As has been pointed out, in the kraft recovery process, the spent liquor is evaporated, burned and caus-

ticized for reuse. When the recovery process is used with a neutral sulfite mill, the spent liquor from the neutral sulfite process is combined with the spent liquor of the kraft process and the combined liquor evaporated, burned and, prior to causticizing, a portion of the sodium is removed.

When the kraft mill is used independent of other mills, sodium sulfate is often added to make up the sodium loss. When this is done, the sulfidity of the regenerated cooking liquor is limited to about 26 percent which necessitates longer cooking and does not provide as high a quality of kraft paper as might be desired. The desired sulfidity for the kraft process is about 30.0 percent and, if no make-up is used, the sulfidity is 20 percent. If neutral sulfite liquor is used to make up the sodium losses in the kraft process and regeneration of the spent liquor, the sulfidity is only about 23 percent, which is unsatisfactory and which necessitates addition of sulfur to achieve the desired sulfidity. On the other hand, when the principles of the invention are used, a kraft liquor may be produced with a sulfidity of 30 percent without difficulty, and a cooking liquor for a neutral sulfite mill may be made up

The term "sulfidity," as used herein, refers to the ratio of the sodium sulfide to sodium sulfide plus sodium carbonate, each compound being expressed as sodium oxide. The foregoing percentages of sulfidity are based upon an assumed sodium loss of 7 percent in the process and a sulfur loss of 35 percent.

In accordance with the present invention, the spent liquor from the neutral sulfite process is added to make up the loss of sulfur in the liquor of the kraft process so that there is an excess of sodium present in the combined liquor for purposes of producing a liquor for the kraft process. A smelt is prepared from the combined liquor, which smelt is dissolved and is processed in such manner that a predetermined amount of sodium may be removed in the form of solid sodium carbonate. The smelt solution may be used in the causticization step of the kraft recovery process. The solid sodium carbonate may be put in solution, sulfited under particular conditions and, after sulfitation, the solution is suitably adjusted for use in a sulfite process.

As in the case of the process described above for direct recovery of spent liquor from the neutral sulfite and acid sulfite processes, in the cross-recovery system of the invention, the liquor from the neutral sulfite process and kraft process are combined, evaporated and burned to produce a smelt which largely comprises sodium sulfide and sodium carbonate, some sodium sulfate being also present. The smelt is dissolved in a predetermined amount of water at a temperature above 100° F. and preferably below 200° F.

In accordance with the principles of the present invention, the amount of semichemical pulp produced in a cross-recovery system by a sulfite process can be greatly increased so as to make the joint operation of a sulfite mill and kraft mill much more satisfactory. It has been pointed out above that known cross-recovery systems are limited in the amount of sulfite pulp which can be produced, the ratio of kraft pulp to sulfite pulp being substantially limited to 4 to 1.

Such substantial improvement in the cross-recovery system is accomplished through partial solution of the smelt produced by burning the combined spent liquor from the kraft mill and sulfite mill. Such partial solution is effected, in accordance with the invention, in such manner that a green liquor of the desired sulfidity is provided for the kraft mill and a residue of substantially pure sodium carbonate remains, which residue, after being put in solution, is sulfited and used in the sulfite mill.

The advantages of such a system over the known cross-recovery system are numerous. In these known systems, the spent liquor from the sulfite mill is used to make up sodium losses and, as a consequence, the sulfidity of the

liquor produced after solubilizing the smelt is not as great as desired. Through the use of the present invention, a liquor of any desired sulfidity may be produced from the smelt for the kraft mill, while at the same time, reducing the ratio between the production of kraft liquor and sulfite liquor, and consequently, increasing the production of sulfite pulp.

In order to effect the partial solution, a particular amount of water is added to provide a solution of desired sulfidity for the kraft mill and the temperature of the solution is raised to above about 100° F. and agitated to assure establishment of equilibrium conditions. The solution is drawn off, causticized in accordance with known practices, and returned to the kraft mill. The residue remaining, which primarily comprises sodium carbonate, is then dissolved and the solution sulfited, whereupon it is returned, ready for use in the sodium base sulfite mill.

It is of greatest importance that the smelt solution be heated above 100° F. At such temperatures, the solubility of sodium carbonate in sodium sulfide solutions is substantially constant. In fact, in the range between 100° F. and 200° F. the solubility of sodium carbonate, at given concentrations of sodium sulfide between 0 and 10 percent, varies less than 2 percent (see Figure 4). At temperatures below about 100° F. the solubility of sodium carbonate rapidly changes and control of the solubilizing of sodium carbonate is difficult and, in fact, from a commercial standpoint, wholly unsatisfactory.

The solubility of sodium carbonate in sodium sulfide solution is illustrated in a graph which is shown in Figure 4 of the drawings. It will be seen that above about 100° F. (38° C.) the solubility of sodium carbonate is substantially constant. Consequently, it will be appreciated that temperature control within relatively wide ranges will provide approximately the same solubilizing of the sodium carbonate. In addition, it will be noted that below about 100° F. (38° C.) the solubility of sodium carbonate changes very rapidly so that commercial utilization of such temperatures is difficult and unfeasible.

From the graph shown in Figure 4, another graph may be drawn with solubility of sodium carbonate and concentration of sodium sulfide as the coordinates in the temperature range of from about 100° F. to about 200° F. Such a graph is shown in Figure 5 of the drawings.

By formulation from these graphs, the particular amount of water to be added to the smelt can be determined to produce a green liquor of desired sulfidity.

Since after burning the smelt will largely comprise sodium carbonate and sodium sulfide, it is assumed for purposes of practical calculation, which is coincident with practical operation, that the smelt only comprises these two compounds, though it will be understood that other compounds may be present in relatively small amounts.

In order to determine the amount of sodium carbonate to be removed in pound-mols per pound-mol of smelt to provide a solution of desired sulfidity, let x be the sulfidity of the smelt. Then let k equal the pound-mols of sodium sulfide in the smelt and a_1 the pound-mols of sodium carbonate in the smelt. By definition;

$$(1) \quad x = \frac{k}{k + a_1}$$

Now, let s equal the sulfidity of the solution, after addition of water to the smelt, and a_2 equal the pound-mols of sodium carbonate in solution. Since all of the sodium sulfide is to be removed from the smelt, then by definition;

$$(2) \quad s = \frac{k}{k + a_2}$$

Solving Equation 1 for a_1 ;

$$(3) \quad a_1 = \frac{k(1-x)}{x}$$

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Solving Equation 2 for a_2 ;

$$(4) \quad a_2 = \frac{k(1-s)}{s}$$

Let y equal the pound-mols of sodium carbonate removed per pound-mol of smelt. Accordingly;

$$(5) \quad y = \frac{a_1 - a_2}{k + a_1}$$

From Equation 1;

$$(6) \quad k + a_1 = \frac{k}{x}$$

Substituting in Equation 5;

$$(7) \quad y = \frac{a_1 - a_2}{k/x}$$

Now substituting for a_1 and a_2 in Equation 7;

$$(8) \quad y = \frac{\frac{k(1-x)}{x} - \frac{k(1-s)}{s}}{k/x}$$

Simplifying Equation 8;

$$(9) \quad y = -\frac{x}{s} + 1$$

Plotting this equation in graph form gives a series of lines, as shown in Figure 6 of the drawings. Thus, knowing the sulfidity of the smelt and the desired sulfidity of a smelt solution, the amount of sodium carbonate to be removed can be readily determined. (In adding the water, the mechanism of the reaction involves dissolution of all of the sodium carbonate in the smelt and recrystallization of the sodium carbonate as a monohydrate. Therefore, the sodium carbonate is removed as a monohydrate.)

In order to add the proper amount of water to provide a green liquor of desired sulfidity and to remove the amount of sodium carbonate determined, as above, a determination can be made with sufficient accuracy for practical operation. First, let x equal the sulfidity of the smelt, a_1 the pound-mols of sodium carbonate in the smelt, and k the pound-mols of sodium sulfide in the smelt, then by definition;

$$(1) \quad x = \frac{k}{k + a_1}$$

Then, let z equal the pound-mols of water in solution and f equal the pound-mols of water in solution added per pound-mol of smelt. Accordingly;

$$(2) \quad f = \frac{z}{k + a_1}$$

If m is the weight fraction of sodium carbonate in solution, the pound-mols in solution being represented by a_2 , then

$$(3) \quad m = \frac{106a_2}{106a_2 + 18z + 78k}$$

Now, let n be the weight fraction of sodium sulfide in solution and therefore

$$(4) \quad n = \frac{78k}{106a_2 + 18z + 78k}$$

From Figure 5 of the drawings, it will be seen that m and n are related by an equation of a straight line. This relationship is approximately

$$(5) \quad m = -1.67n + .32$$

If s is the sulfidity of the solution,

$$(6) \quad s = \frac{k}{k + a_2}$$

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Substituting for m and n in Equation 5 from Equations 3 and 4,

$$(7) \quad \frac{106a_2}{106a_2 + 18z + 78k} = -\frac{1.67 \cdot 78 \cdot k + .32}{106a_2 + 18z + 78k}$$

Solving for a_2 ;

$$(8) \quad 72a_2 = -105k + 5.75z$$

From Equations 1 and 2

$$(9) \quad \frac{z}{k} = \frac{f}{x}$$

Then, from Equations 6, 8 and 9

$$(10) \quad f = \frac{x}{s}(5.73s + 12.5)$$

In the temperature range of from about 100° F. to about 200° F., the sodium carbonate in the solid phase is in the monohydrate form, and accordingly, a certain amount of water is required by the sodium carbonate. As previously shown, the amount of sodium carbonate removed in pound-mols per pound-mol of smelt is expressed by the following equation:

$$(11) \quad y = -\frac{x}{s} + 1$$

Accordingly, the amount of water required for the sodium carbonate in the remaining smelt in pound-mols per pound of smelt is:

$$(12) \quad y \text{ or } -\frac{x}{s} + 1$$

Then the total amount of water to be added, designated by y' , is:

$$(13) \quad y' = -\frac{x}{s} + 1 + f, \text{ or } y' = \frac{x}{s}(5.73s + 11.5) + 1$$

This equation may be illustrated graphically and is shown in Figure 7 of the drawings. Accordingly, if the sulfidity of the smelt is determined and the desired sulfidity of the solution is known, the amount of water to add can be determined, providing the solution is at a temperature between about 100° F. and about 200° F.

By way of example, a kraft mill operating at a production rate of 100 ton of pulp per day and a neutral sulfite mill operating at 70 ton per day may be operated in conjunction with one another. By heretofore known processes, the neutral sulfite mill has been limited to a production of about 25 tons per day.

The liquors of the two mills are combined, evaporated and burned. In evaporation, the loss of sodium and sulfur is negligible, the loss being, in each case, about one percent. However, in combustion, the sodium loss is about 4 percent, while the sulfur loss is about 32 percent.

The resulting smelt is about 21 percent sodium sulfide, about 77 percent sodium carbonate, and about 2 percent sodium sulfate. Thus, the sulfidity of the smelt is about 27, all expressed as Na_2O . If the desired sulfidity of the green liquor is 30, then from the graph shown in Figure 7, 12.9 pound-mols of water is added for each pound-mol of smelt. The water is added at a temperature of 150° F. and the solution agitated for about fifteen minutes.

The solution is then filtered off and causticized, in accordance with normal practice. The remaining solids largely comprise sodium carbonate which are dissolved in water and sulfited. During sulfitation sodium carbonate is added and, after sulfitation, adjustment of pH is effected to provide the desired cooking liquor.

In the event that some sodium sulfide is undissolved in the solids remaining after filtering, the concurrent tower operation is to be preferred over the normal counter-current tower operation. It will be understood, however, that either means of sulfitation may be employed.

From the foregoing, it will be seen that the equations and graphs are approximations of the manner of effecting partial solution of sodium carbonate and that some adjust-

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ment must necessarily be made under various operating conditions within the scope of this invention. However, such adjustment, in view of the foregoing disclosure, is readily within the skill of the art.

In accordance with the principles of the present invention, recovery of sodium base sulfite liquor can be effected either in the operation of a sulfite mill independently or in conjunction with a kraft mill. Such recovery can now be done economically and practically so that greater utilization of the sodium base sulfite processes can now be made. Furthermore, the present cross-recovery arrangements can be expanded without difficulty to make for increased production of sodium base sulfite pulp.

The various features of the invention believed to be new are set forth in the following claims.

We claim:

1. In a process for recovering spent liquor after sodium base, sulfite treatment of wood to provide a high quality liquor with low thiosulfate content for treating wood, the steps of concentrating the spent liquor, burning the spent liquor to form a smelt, said burning being done under conditions which minimize the removal of sulfur and convert a major portion of the sulfur in the liquor to sodium sulfide in the smelt, dissolving said smelt to provide an aqueous solution having a pH in excess of 11.0 and a sodium sulfide concentration of less than about 1.2 mols per liter, treating said solution to provide the liquor with low thiosulfate content by sulfiting said solution with sulfur dioxide at a temperature between about 60° C. and 100° C. so as to reduce the pH to below 9.5 and maintain the pH of the solution above 7.0, said aqueous solution and said sulfur dioxide flowing concurrently to minimize the effective contact between the sulfur dioxide and the hydrogen sulfide produced during sulfitation.

2. In a process for recovering spent liquor after sodium base, sulfite treatment of wood to provide a high quality liquor with low thiosulfate content for treating wood, the steps of concentrating the spent liquor, burning the spent liquor to form a smelt, said burning being done under conditions which minimize the removal of sulfur and convert a major portion of the sulfur in the liquor to sodium sulfide in the smelt, dissolving said smelt to provide an aqueous solution having a pH in excess of 11.0 and a sodium sulfide concentration of less than about 1.2 mols per liter, and treating said solution to provide the liquor with low thiosulfate content by sulfiting said solution with sulfur dioxide at a temperature between 60° C. and 100° C., reducing the pH of the solution to below 9.5 and maintaining the pH of the solution above 8.5, said aqueous solution and said sulfur dioxide flowing concurrently to reduce the effective contact between the sulfur dioxide material and the solution as the pH of the solution is reduced.

3. In a process for recovering spent liquor after sodium base, sulfite treatment of wood to provide a high quality liquor with low thiosulfate content for treating wood, the steps of concentrating the spent liquor, burning the spent liquor to form a smelt, said burning being done under conditions which minimize the removal of sulfur and convert a major portion of the sulfur in the liquor to sodium sulfide in the smelt, dissolving said smelt to provide an aqueous solution having a pH in excess of 12.0 and a sodium sulfide concentration of less than about 1.2 mols per liter, and treating said solution to provide the liquor with low thiosulfate content by sulfiting said solution with sulfur dioxide at a temperature between 60° C. and 100° C. so as to reduce the pH to about 9.0, and reducing the effective contact between the sulfur dioxide and the solution as the pH is reduced, said aqueous solution and said sulfur dioxide flowing concurrently so that the sulfur dioxide is substantially out of contact with said solutions at the lowest pH of the solution.

4. In a process for recovering spent liquor after sodium base, sulfite treatment of wood to provide a high quality liquor with low thiosulfate content for treating wood,

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the steps of concentrating the spent sulfite liquor, burning the spent liquor to form a smelt, said burning being done under conditions which minimize the removal of sulfur and convert a major portion of the sulfur in the liquor to sodium sulfide in the smelt, dissolving said smelt to provide a dilute aqueous solution having a pH in excess of 11.0 and a sodium sulfide concentration of less than about 1.2 mols per liter, treating said solution to provide the liquor with low thiosulfate content by sulfiting said aqueous solution at a temperature between 60° C. and 100° C. by flowing said solution through a packed tower concurrently with dilute sulfur dioxide gas, and removing said solution from effective contact with the spent gas at a pH in excess of 7.0.

5. In a process for recovering spent liquor after sodium base, sulfite treatment of wood to provide a high quality liquor with low thiosulfate content for treating wood, the steps of concentrating the spent sulfite liquor, burning the spent liquor to form a smelt, said burning being done under conditions which minimize the removal of sulfur and convert a major portion of the sulfur in the liquor to sodium sulfide in the smelt, dissolving said smelt to provide a dilute aqueous solution of sodium sulfide having a pH in excess of 11.0 and a sodium sulfide concentration of less than about 1.2 mols per liter, treating said solution to provide the liquor with low thiosulfate content by sulfiting said solution at a temperature between 60° C. and 100° C. by flowing said solution through a packed tower concurrently with dilute sulfur dioxide gas and removing said solution from effective contact with the spent gas at a pH of about 9.0, the sulfur dioxide being at least about 90 percent utilized when the pH of said solution is about 9.0.

6. In a process for recovering spent liquor after sodium base, sulfite treatment of wood to provide a high quality liquor with low thiosulfate content for treating wood, the steps of concentrating the spent sulfite liquor, burning the spent liquor to form a smelt, said burning being done under conditions which minimize the removal of sulfur and convert a major portion of the sulfur in the liquor to sodium sulfide in the smelt, dissolving said smelt to provide a dilute aqueous solution of sodium sulfide having a pH in excess of 11.0 and a sodium sulfide concentration of less than about 1.2 mols per liter, treating said solution to provide the liquor with low thiosulfate content by sulfiting said aqueous solution at a temperature between 60° C. and 100° C. by flowing said solution through a packed tower concurrently with a dilute sulfur dioxide gas, the ratio of the diluting gas to sulfur dioxide gas being in the range from about 5:1 to about 20:1, and removing said solution from the spent gas at a pH below 9.5 and above 8.5, the rate of flow of said solution and said gas being adjusted to substantially utilize said gas at the time that the pH of said solution is in the range between 9.5 and 8.5.

7. In a process for recovering spent liquor after sodium base, sulfite treatment of wood to provide a high quality liquor with low thiosulfate content for treating wood, the steps of concentrating the spent sulfite liquor, burning the spent liquor to form a smelt, said burning being done under conditions which minimize the removal of sulfur and convert a major portion of the sulfur in the liquor to sodium sulfide in the smelt, dissolving said smelt to provide a dilute aqueous solution of sodium sulfide having a pH in excess of 12.0 and a sodium sulfide concentration of less than about 1.2 mols per liter, treating said solution to provide the liquor with low thiosulfate content by sulfiting said solution at a temperature between 60° C. and 100° C. by flowing said solution through a packed tower concurrently with a dilute sulfur dioxide gas, removing said solution from said gas at a pH of about 9.0.

8. In a process for recovering spent liquor after sodium base, sulfite treatment of wood to provide a high quality liquor with low thiosulfate content for treating wood, the steps of concentrating the spent sulfite liquor, burning the

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spent liquor to form a smelt, said burning being done under conditions which minimize the removal of sulfur and convert a major portion of the sulfur in the liquor to sodium sulfide in the smelt, dissolving said smelt to provide a dilute aqueous solution of sodium sulfide having a pH in excess of 12.0, the concentration of sodium sulfide being less than 1.2 mols per liter, treating said solution to provide the liquor with low thiosulfate content by sulfiting said solution at a temperature between 60° C. and 100° C. by flowing said solution through a packed tower concurrently with a dilute sulfur dioxide gas, the ratio of diluting gas to sulfur dioxide gas being in the range from about 5:1 to 20:1, removing said solution from said gas

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at a pH of about 9.0, the rate of flow of said solution and said gas being adjusted so that the sulfur dioxide is more than about 90 percent utilized when the solution is at a pH of about 9.0.

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