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TREATMENT OF SPENT SULFITE LIQUOR

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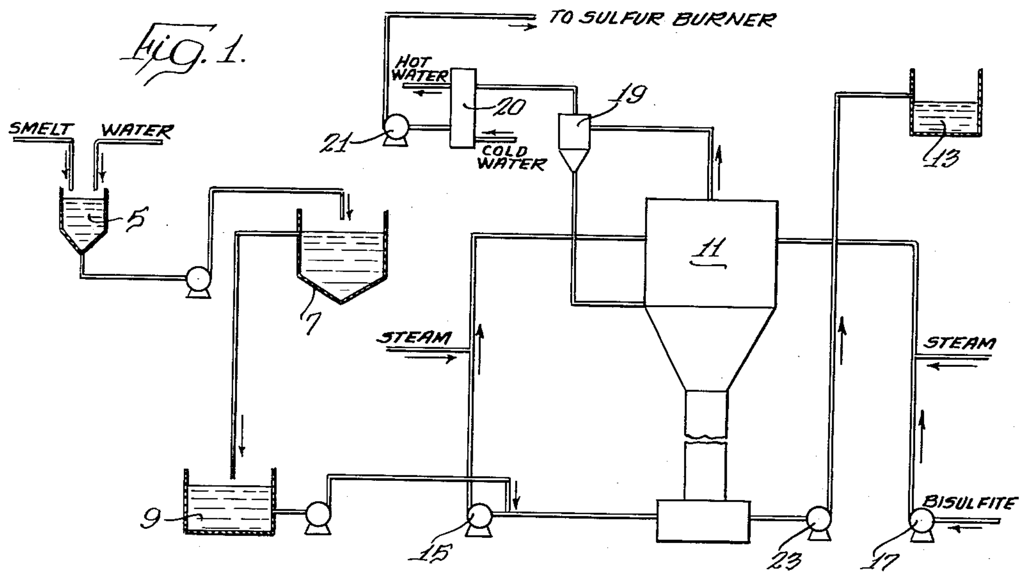
Fig. 1.



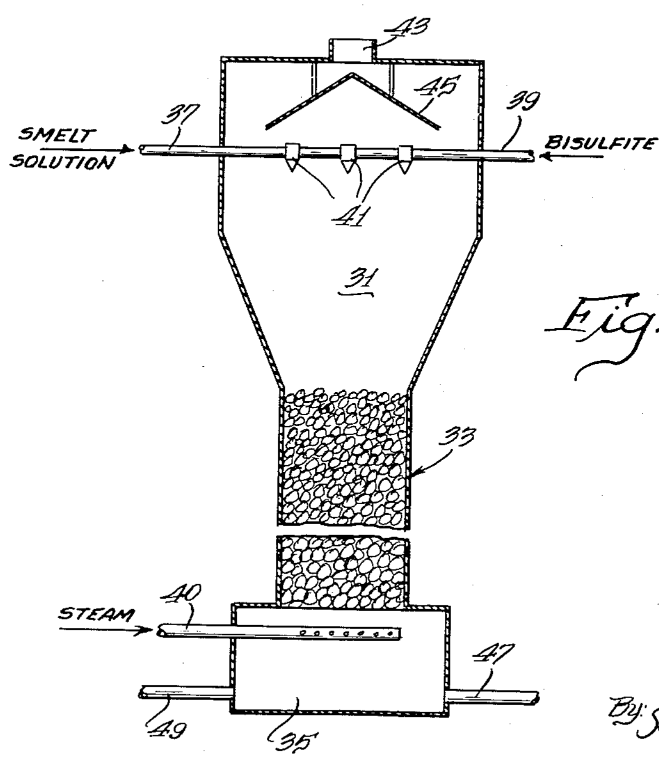


Fig. 2.

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TREATMENT OF SPENT SULFITE LIQUOR

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The present invention relates generally to the preparation of wood pulp by a sulfite process employing a sodium base liquor. It is more particularly related to improvements in the preparation of cooking liquor for the sulfite process from spent liquor.

Paper and paper products are manufactured from wood which has been converted into pulp. Wood pulp may be prepared by one of a number of processes. Generally speaking, wood pulp is either prepared by a mechanical process, or a chemical process. Chemical processes include the acid sulfite, neutral sulfite, sulfate and soda processes. A more recently employed process is the semichemical pulping process which has achieved substantial importance because of the high yield of pulp obtainable therefrom. Since in the semichemical process, the wood is subjected to a milder treatment than in the chemical processes, it is readily understood how higher yields result.

Wood treated in accordance with the semichemical pulping process may be digested under substantially neutral conditions with a sodium compound. A well known process utilizes sodium sulfite in the cooking liquor in connection with digestion of the pulp. This invention primarily relates to the recovery of the spent liquor, i.e. the liquor remaining after digestion and removal of the pulp.

While various processes have been developed for recovering sodium base, spent sulfite liquor, they have not all been economical to practice nor have they provided a cooking liquor of high quality. Furthermore, previously known processes have required substantial capital investment for recovery of the liquor.

The pulp produced by the neutral sulfite semichemical pulping processes possesses strength and good bleachability characteristics. These and other characteristics, in view of the high yield, have established neutral sulfite semichemical pulp for use in the manufacture of paper and paperboard products. The semichemical pulp has been combined with other pulps in the manufacture of high grade paper, such as book paper.

In order to provide an overall process which is commercially practicable, various attempts have been made to recover the spent liquor by concentration and burning to provide a smelt. The smelt is dissolved to furnish an aqueous solution which is then treated with sulfur dioxide to form sodium sulfite. However, this technique as usually practiced in the past has resulted in the formation of excessive amounts of thiosulfates and other polythionic compounds which are not effective in digestion and result in a "dead load" in the system.

Attempts have also been made to oxidize smelt solutions in order to prepare a cooking liquor. These attempts have not resulted in a commercially practicable process for the paper industry.

Similarly, carbonation processes for recovering spent liquor have not been adopted.

A suitable recovery method for spent liquor from a sodium base, sulfite pulping process has been discovered and it is set forth in United States patent application, Serial No. 382,678, filed September 28, 1953, now United States Patent No. 2,802,791, issued August 3, 1957, assigned to the assignee of this invention. This process involves the treatment of smelt recovered from spent sulfite liquor. The smelt is dissolved and treated under particular conditions to minimize the contact between hydrogen sulfide and sulfur dioxide.

We have now discovered a new method whereby a cooking liquor of high quality for a sodium base, sulfite pulping process can be prepared from spent liquor in a simple and economical manner without substantial formation of thiosulfates and other polythionic compounds so that a high quality liquor results. In addition, by this method, hydrogen sulfide from a sulfitation operation may be recovered in a concentrated form. The recovered hydrogen sulfide is converted to sulfur dioxide and then to sodium bisulfite, the sulfitation agent of the method. The method may be carried out in a continuous or batch operation and may be utilized in the preparation of acid sulfite liquor or neutral sulfite liquor.

In the method, sodium bisulfite, in aqueous solution, is reacted with an aqueous smelt solution under particular conditions to provide a high quality cooking liquor.

A main object of the present invention is to provide an improved method for handling the spent liquor from a sodium base, sulfite pulping process.

Another object of this invention is to provide a high quality cooking liquor from spent liquor from a sodium base, sulfite pulping process by direct sulfitation with sodium bisulfite.

It is also an object of this invention to provide a cooking liquor, substantially free from sodium thiosulfate or other polythionic compounds, for the sodium base, sulfite semichemical pulping process or for the sodium base acid sulfite pulping process, through the use of sodium bisulfite.

Further objects of this invention will be obvious from a study of the accompanying drawing and following disclosure. In the drawing:

FIGURE 1 is a schematic drawing of a portion of a recovery system which may be employed in the recovery of spent sulfite liquor.

FIGURE 2 is a schematic drawing of a conversion tower included in the system shown in FIGURE 1.

In accordance with the invention, spent liquor from a sodium base, sulfite pulping process is concentrated to form about 55 to about 70 percent solids content in a suitable manner. The concentrated liquor is then burned under reducing conditions so as to limit the removal of sulfur as much as possible. In this connection, a major portion of the sulfur should be retained in the resulting smelt. The smelt formed by burning primarily comprises sodium sulfide and sodium carbonate. The smelt is then dissolved to form an aqueous solution of the sodium sulfide and sodium carbonate.

The sodium sulfide and sodium carbonate are then converted to the desired sodium sulfide. This conversion is effected by direct sulfitation of the aqueous smelt solution with sodium bisulfite. The reaction occurring during the sulfitation may be represented by the following equations:

$$Na_2S+NaHSO_3=Na_2SO_3+NaHS$$
$$NaHS+NaHSO_3=Na_2SO_3+H_2S$$
$$Na_2CO_3+NaHSO_3=Na_2SO_3+NaHCO_3$$
$$2NaHCO_3=Na_2CO_3+CO_2+H_2O$$

Thus, not only is the sodium sulfide converted to sodium sulfite, but so also is sodium carbonate.

Since an equilibrium exists between sodium bisulfite and sulfur dioxide-sodium sulfite and since hydrogen sulfide reduces sulfur dioxide, a condition exists which results in the formation of sodium thiosulfate. This may be represented by the following equations:

$$2NaHSO_3=Na_2SO_3+SO_2+H_2O$$
$$SO_2+2H_2S=3S+2H_2O$$
$$Na_2SO_3+S=Na_2S_2O_3$$

Accordingly, it appears that the presence of hydrogen

sulfide in the solution influences the final concentration of thiosulfates and other polythionic compounds. We establish conditions which minimize contact between sulfur dioxide present and hydrogen sulfide, and this minimizes thiosulfate formation.

Heretofore, it was thought that the mode of formation of sodium thiosulfate was according to the following equation:

$$Na_2SO_3+SO_2=Na_2S_2O_3+O_2$$

Since sulfur dioxide is the common sulfitation agent in the conventional commercial process, formation of sodium thiosulfate during direct sulfitation has been generally accepted.

From the foregoing, however, the formation of thiosulfate depends upon the initial reaction between the hydrogen sulfide and the sulfur dioxide, with the resulting formation of elemental sulfur. Consequently, when the contact between these two agents is minimized, the formation of thiosulfate is accordingly minimized. It has been found that sulfur dioxide does not react with sodium sulfide, and will not react with sodium hydrosulfide to form thiosulfate.

The smelt from the furnace should have a sulfidity of between about 30 percent and about 70 percent. The term "sulfidity" refers to the molar ratio of sodium sulfide in the smelt to the sum of the sodium sulfide and the sodium carbonate in the smelt. Of course, this ratio is multiplied by 100 to provide the percent.

In addition, the reduction of the smelt must be greater than 85 percent, the percent reduction being the molar ratio of sodium sulfide to sodium sulfide plus sodium sulfate, times 100.

It is within the skill of the art to provide burning conditions in a recovery furnace so as to give a smelt having the desired degree of reduction and the desired sulfidity.

As has been previously indicated, this invention is based upon the establishment of certain conditions for minimizing the contact between the hydrogen sulfide and sulfur dioxide, when a smelt solution from spent sulfide liquor is reacted with a sodium bisulfide solution so as to provide a liquor of high quality. For purposes of commercial operation, the gross quality of the liquor should be in excess of 85 percent and the net quality should exceed 80 percent. At lower liquor qualities, the recovery process is not commercially feasible and the digestion of the pulp is not as satisfactorily carried out.

The term "gross quality" refers to the molar ratio of the amount of sodium sulfite to the amount of sodium sulfite plus the amount of sodium thiosulfate formed in the reaction. The term "net quality" refers to the amount of sodium sulfite recovered from the sodium sulfide in the smelt to the amount of such sodium sulfite plus the amount of sodium thiosulfate.

The smelt solution should be at a boiling temperature and the contact between the solution and sodium bisulfite should be under conditions which establish a large surface area and immediate stripping of any formed hydrogen sulfide gas. In this connection, in a batch operation, the boiling rate of the smelt solution should exceed 40 grams of vapor per minute per square foot of surface area to obtain 100 percent conversion of the sodium sulfide in the smelt solution. While lower boiling rates can be tolerated at lower degrees of conversion to provide the desired net quality, i.e. quality in excess of 80 percent, a boiling rate of less than about 15 grams of vapor per minute per square foot of surface area is not satisfactory.

Because of the inherent difficulties in carrying out the batch operation, the preferred method for practicing this invention involves mixing of the smelt solution, at high temperature, for a short period and then spraying the solution into an open chamber. In this connection, the time of contact between the solutions should not exceed five seconds, and the time is preferably less than .1 second.

The solution is sprayed, as indicated, and stripping steam is flowed through the spray at a rate in excess of

25 pound moles of steam per pound mole of sodium sulfide in the smelt solution, i.e. the total amount of stripping steam employed should be at least 25 pound moles of steam per pound mole of sodium sulfide in the smelt solution. For the most satisfactory operation, the stripping steam should exceed 40 pound moles of steam per pound mole of sodium sulfide. In order that the steam can act effectively, the spray should establish a surface area on the drops in excess of 100 square feet per minute per gallon of liquor sprayed. The area of the droplets and the amount of stripping steam should be adjusted so that the hydrogen sulfide in the resulting liquor is retained at a ratio of less than .14 mole per mole of sodium sulfide introduced in spray form and preferably less than .12 mole per mole of sodium sulfide introduced. If the retained hydrogen sulfide is present in a ratio of less than .12 mole per mole of sodium sulfide in the liquor sprayed, and other conditions are maintained, the net quality will exceed about 85 percent.

The concentration of sodium sulfide in the smelt solution should be no more than about 2 gram moles per liter, the maximum concentration of sodium sulfide being controlled by the solubility limit of sodium sulfite in the resulting liquor.

In order to provide satisfactory continuous operation, the mole ratio of the amount of sodium bisulfite to the amount of sodium sulfite plus sodium bisulfite in the solution which is mixed with the smelt solution should not be greater than about .90. The use of higher ratios results in a lower liquor quality. Of course, too low a ratio results in inefficient operation. At a ratio above .7 excessive sulfur losses occur in condensation of the exhausted gases.

In order to effect most satisfactory treatment of the smelt solution, the pH of the aqueous smelt solution should be above about 11.0, and preferably above 12.0. Suitable adjustment of pH may be effected by addition of chemicals during burning or in the dissolving of the smelt.

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

Compound:	Lbs.
Na_2SO_3	340
Na_2CO_3	24
$NaHCO_3$	51
$Na_2S_2O_3$	41
Na_2SO_4	14
Total	470

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

The contents of the digester are discharged into a blow tank and the pulp and spent liquor are separated. This is done in accordance with well known practices.

The spent sulfite liquor, which is to be recovered in accordance with this invention, is then concentrated. After concentration, the liquor is a combustible concentrate and will ordinarily contain about 65 percent solids. It is then passed to and burned in a furnace, such as a Babcock and Wilcox furnace, to provide the desired reduction and a smelt having the required sulfidity.

The smelt from the furnace is dissolved in water in tank 5 to provide the dilute aqueous solution which is to be sulfited. This solution is passed to clarifier 7. In the clarifier, the solution is separated from any undissolved solids. It is then pumped to a storage tank 9.

An analysis of a typical smelt solution of this invention leaving the dissolving mask 5 is given below. The analysis is on the basis of one ton of pulp.

Compound:	Lbs.
Na_2S	147
NaHS	30
NaOH	22
Na_2CO_3	114
Na_2SO_4	14
Total	327

The smelt solution is then pumped to a conversion tower **11** in which the solution is converted to the desired treating liquor. Upon suitable conversion, the liquor is then stored in a tank **13** for use in the digester.

Conversion tower **11** may be of the type shown in FIGURE 2 for continuous operation. The regeneration system of FIGURE 2 may be used in the preparation of either neutral sulfite or acid sulfite liquor.

As shown in FIGURE 1, the smelt solution, or green liquor, is introduced into a pump **15** and is mixed with steam to heat it, whereupon it is introduced into the conversion tower **11**. Sodium bisulfite liquor (as previously pointed out, this liquor includes sodium sulfite), which has been heated by steam, is also pumped from a pump **17** into the conversion tower **11**. The gases which leave the conversion tower are introduced into a cyclone separator **19**, which returns any liquid to the tower **11**. The gases leave the cyclone **19** and enter a condenser **20** and the remaining gas, referred to as sour gas, is passed through a fan **21** to a sulfur burner (not shown). A portion of the liquor which has been recovered as cooking liquor leaves the regeneration system **11** through the pump **23**, and another portion of the liquor is mixed with the green liquor and introduced into the pump **15**. Thus, some of the liquor is recycled.

The conversion tower **11** basically comprises three sections, they being a spray chamber **31**, a packed section **33** and a sump **35**. The lowermost section is the sump **35**. Superimposed thereon is the packed section **33**, and above the packed section is the spray chamber **31**. The packed section **33** may be filled with any of several commercially available packing materials, such as partition rings, spiral tiles, Raschig rings, Berl saddles, wire-mesh packings, or other suitable types of conventional absorption tower packing material.

The smelt solution enters conversion tower **11** through pipe **37**. The sodium bisulfite solution enters the conversion tower **11** through pipe **39**. The pipes **37** and **39** each connect to nozzles **41** which spray the mixed liquor and bisulfite solution into the spray chamber. The sprayed liquor then passes through the packed section **33** to the sump **35**.

The tower is operated at the boiling point of the combined spray, that is, at least about 212° F. to 214° F. under atmospheric pressure conditions. Preferably, sufficient extra heat is continuously added in the liquor and thereby to the spray to provide an increased boiling rate.

During passage of the boiling spray down through the packing, it countercurrently contacts steam which has entered the sump **35** of the conversion tower **11**. Steam entering through line **40** passes up through the packed section **33** of the tower **11**. The steam is at a temperature which is a function of the pressure conditions in the tower and the steam aids in stripping hydrogen sulfide formed during the reaction between the sodium bisulfite and the sodium sulfide in the spray. The steam has the additional effect of aiding in maintaining the downflowing spray solution at the desired temperature.

Hydrogen sulfide and other effluent gasses pass from the tower through stack **43** after flowing around the baffle **45**. Baffle **45** is provided so as to substantially eliminate exiting of inflowing bisulfite solution spray and smelt solution spray before their passage down through the packed section to the sump **35**.

When the liquor reaches the sump **35**, it passes from the tower **11** through pipes **47** and **49**, pipe **47** conducting

the liquor to the storage tank **13** and pipe **49** conducting the liquor to the pump **15** for recycling.

It will be understood that the tower shown in FIGURE 2 may be operated on a batch basis by filling the sump **35** melt solution.

EXAMPLE I

An eight inch stainless-steel conversion tower of the type shown in FIGURE 2 was operated on a batch basis in accordance with the conditions set forth in Table I below.

Table I

BATCH BISULFITE PROCESS

[Spray method]

Run	I	II
Smelt Solution:		
Volume, liters	7.0	5.0
$Na_2S_2O_3$, g. moles	0.035	0.040
Na_2SO_3, g. moles	0.042	0.040
Na_2S, g. moles	0.588	2.323
Na_2CO_3, g. moles	0.721	2.315
Bisulfite solution:		
Volume, liters	12.2	6.1
Na_2SO_3, g. moles	0.037	2.075
$NaHSO_3$, g. moles	2.365	9.250
Reaction solution:		
Reacting time, min	120	80
Volume,[1] liters	35.7	15.2
pH	8.13	8.46
$Na_2S_2O_3$, g. moles	0.071	0.639
Na_2SO_3, g. moles	2.538	10.60
$NaHCO_3$, g. moles		0.350
Recycling rate, gal./min	1	1
Na_2S conversion, mole percent	100	100
Na_2CO_3 conversion, mole percent	100	92.5
Gross quality, mole percent	98.6	93.5
Net quality, mole percent	96.5	87.8

[1] Estimated volume based on sodium balance.

The tower was operated at boiling temperature for the indicated time.

The beneficial effect of increased interfacial area and high boiling rate is confirmed by these runs. The above batch process was carried out under conditions of vigorous boiling, that is, with increased heat added to the smelt solution-bisulfite solution mixture over that necessary to achieve minimal boiling of the combined solution.

EXAMPLE II

In a commercial unit, the smelt includes the following material in the specified amounts:

	Moles per ton
Sodium sulfide	2.90
Sodium sulfate	.35
Sodium carbonate	1.78

About 488 pounds of this smelt is introduced into the dissolving tank **5** at about 1800° F. In clarification, about one percent of the chemicals is lost. Water is added, about 4940 pounds being added to the smelt at 120° F. The clarified green liquor is discharged at about 194° F. and conducted to the conversion tower **11** which, in this case, is operated under atmospheric pressure. The flow rate is 46 gallons per minute.

The spray nozzle pressure in the conversion tower is 50 p.s.i. and the smelt solution is heated to a temperature of 250° F. The cooking liquor is recycled from the sump **35** so that the recycled liquor has a ratio to the entering green liquor of 3 to 1, by volume.

Bisulfite solution is introduced at a ratio of bisulfite to sodium sulfite of 7 to 3, on a molar basis. The bisulfite liquor is at a temperature of 205° F. at the pulp **17**. The liquor has the following composition:

	Pounds
Na_2SO_3	485
$NaHSO_3$	933
$Na_2S_2O_3$	193
Na_2SO_4	99
Water	11,400

Steam is introduced through pipe **40** at the rate of

800 pounds per mole of sodium sulfide. The rate of liquor flow in the tower is 1000 pounds per hour per square foot of spray chamber cross section. The conversion of sodium sulfide is 100 percent and the conversion of sodium carbonate is 80 percent, on a molar basis. The data for the various liquor streams are set forth below:

	Green Liquor	Bisulfite Liquor	Exit liquor		
			for Recycling	for Bisulfite	for Cooking
Na_2S, moles/ton	2.88				
Na_2SO_3, moles/ton		3.85	11.13	8.11	3.94
$NaHSO_3$, moles/ton		8.98			
$Na_2S_2O_3$, moles/ton		1.22	1.67	1.22	0.59
Na_2SO_4, moles/ton	0.34	0.70	0.96	0.70	0.34
Na_2CO_3, moles/ton	1.77		0.10	0.07	0.03
$NaHCO_3$, moles/ton			0.47	0.34	0.16
Chemicals, lb./ton	460	1,710	1,850	1,348	657
Water, lb./ton	5,330	11,530	15,830	11,530	5,610
Liquor, lb./ton	5,790	13,240	17,680	12,880	6,270
Flow, gal./ton	622	1,485	1,985	1,445	702
Na_2S reacted, moles/ton	2.88				
Na_2S conversion, mole percent	100				
Na_2CO_3 reacted, moles/ton	1.42				
Na_2CO_3 conversion, mole percent	80.2				
Liquor quality, mole percent	86.9				
Na_2SO_3 formed, moles/ton	8.20				
$Na_2S_2O_3$ formed, moles/ton	0.59				
Gross quality, moles percent	93.3				
Na_2SO_3 formed from Na_2S, moles/ton	5.36				
Net Quality, mole percent	90.2				

The overall data on the operation of the conversion tower **11** for a commercial operation is set forth below:

		Lb./ton pulp
Green liquor		5,790
Bisulfite liquor (205° F.)		13,240
Na_2SO_3	485.	
$NaHSO_3$	935.	
$Na_2S_2O_3$	193.	
Na_2SO_4	99.	
Water	11,530.	
Bisulfite-sulfite ratio	7:3 by mole.	
Flow	1,485 gal./ton or 103 gal./min.	
Recycling liquor (212° F.)		17,680
Na_2SO_3	1,400.	
$Na_2S_2O_3$	264.	
Na_2SO_4	136.	
Na_2CO_3	11.	
$NaHCO_3$	39.	
Water	15,830.	
Recycling-green liquor ratio	3:1 by volume.	
Flow	1,985 gal./ton or 138 gal./min.	
Steam at atmospheric pressure		2,600
Total input		39,310
Exit liquor (215° F.)		36,830
Na_2SO_3	2,920.	
$Na_2S_2O_3$	550.	
Na_2SO_4	283.	
Na_2CO_3	21.	
$NaHCO_3$	81.	
Water	32,970.	
Liquor distribution:		
Cooking	17%.	
Bisulfite	35%.	
Recycling	48%.	
Exit gas (210° F.)		2,455
H_2S	85.	
CO_2	70.	
H_2O	2,300.	
Total output		39,285
Spray chamber dimensions	14 ft. D. x 14 ft.	
Packed section	4.5 ft. D. x 10 ft.	
Sump	6 ft. D. x 5 ft.	
Sour gas exit	10-in.	
Packing	2-in. glazed porcelain Raschig rings.	
Steam rate, packed section	280 lb./(hr.) (sq. ft.).	
Liquor rate, spray chamber	1,000 lb./(hr.) (sq. ft.).	
Liquor rate, packed section	10,000 lb./(hr.) (sq. ft.).	
Spray rate	350,000 sq. ft./min.	

It has been found that in order to effectively use sodium bisulfite as a sulfiting agent to produce a high quality liquor, certain basic conditions should be established. These various conditions are inter-related and can be varied within the specified limits, in relation to one another, to provide the desired results of this invention. While the operating conditions can be varied, certain conditions appear to be of substantial importance. In this connection, the reaction between the bisulfite solution and the smelt solution should occur under high boiling rate conditions. The time of contact between bisulfite solution and the smelt solution should be minimized which, of course, is promoted by the establishment of the high boiling conditions. To aid in minimizing this contact time, the spray area, i.e. the droplets discharged from the nozzles, is preferably increased as much as possible and stripping steam is employed over this area in a particular amount. The concentration of sodium sulfide should be maintained at a relatively low level in the smelt solution and the concentration of sodium ion should be also maintained at a comparatively low level. If the proper smelt has been provided, a liquor having high net quality and high gross quality can be provided. Of course, the pH of the solutions should be above 7.0 and the pH of the initial smelt solution is desirably above 11.0.

As before indicated, the present invention may be practiced by utilizing spent liquors from either the sodium base, neutral sulfite pulping process or the sodium base acid sulfite pulping process. In the vent that the batch or continuous method of recovery is utilized with spent liquor from the acid sulfite pulping process, the aqueous liquor recovered from the conversion tower **11** may be subjected to a further treatment with sulfur dioxide to increase its acidity. This may be done in another conversion tower by further sulfitation with sulfur dioxide gas.

In the foregoing discussion, continuous and batch processes have been described for recovering spent liquors from neutral sulfite and acid sulfite pulping processes in an easy and economical manner. The processes of this invention are independent of other processes.

It will be evident that various modifications in the procedural steps and/or equipment for carrying them out can be made in the processes described without departing from the scope of the present invention.

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

We claim:

1. In a sodium base, sulfite pulping process, the improvement which comprises the steps of concentrating the spent liquor from the pulping process, burning the concentrated liquor to provide a smelt having a sulfidity of between about 30 percent and about 70 percent, the reduction of said smelt being in excess of 80 percent, dissolving said smelt to provide an aqueous solution and boiling said solution having a sulfidity between about 30 percent and about 70 percent at a rate in excess of 15 grams of vapor per minute per square foot of surface area during addition of sodium bisulfite solution to said aqueous solution in an amount sufficient to provide sufficient sodium bisulfite to react with substantially all of the sodium sulfide in said aqueous solution, whereby direct sulfitation occurs, and rapidly removing the hydrogen sulfide from the resulting boiling solution, whereby formation of sodium thiosulfate and associated substances is substantially avoided.

2. In a sodium base, sulfite pulping process, the improvement which comprises the steps of concentrating the spent liquor from the pulping process, burning the concentrated liquor to provide a smelt having a sulfidity of between about 45 percent and about 70 percent, the reduction of said smelt being in excess of 85 percent, dissolving said smelt to provide an aqueous solution and boiling said solution having a sulfidity of between about 45 percent and about 70 percent at a rate in excess of 40 grams of vapor per minute per square foot of surface area during addition of sodium bisulfite solution to said aqueous solution in an amount sufficient to provide sufficient sodium bisulfite to react with substantially all of

the sodium sulfide in said aqueous solution, whereby direct sulfitation occurs, and rapidly removing the hydrogen sulfide from the resulting boiling solution, whereby formation of sodium thiosulfate and associated substances is substantially avoided.

3. In a sodium base, sulfite pulping process, the improvement which comprises the steps of concentrating the spent liquor from the pulping process, burning the concentrated liquor to provide a smelt having a sulfidity of between about 30 percent and about 70 percent, the reduction of said smelt being in excess of 80 percent, dissolving said smelt to provide an aqueous solution and mixing said aqueous solution having a sulfidity of between about 30 percent and about 70 percent with a sodium bisulfite solution in an amount sufficient to provide sufficient sodium bisulfite to react with substantially all of the sodium sulfide in said aqueous solution for a total contact time of less than 5 seconds at a boiling temperature, whereby direct sulfitation occurs, spraying the mixed solution, and passing stripping gas through the sprayed mixed solution, the amount of said gas exceeding 25 pound moles per pound mole of sodium sulfide in said aqueous solution, whereby formation of sodium thiosulfate and associated substances is substantially avoided.

4. In a sodium base, sulfite pulping process, the improvement which comprises the steps of concentrating the spent liquor from the pulping process, burning the concentrated liquor to provide a smelt having a sulfidity of between about 30 percent and about 70 percent, the reduction of said smelt being in excess of 85 percent, dissolving said smelt to provide an aqueous solution having a sulfidity of between about 30 percent and about 70 percent, the concentration of sodium siulfide in said smelt solution being less than about 2.0 gram moles per liter and mixing said aqueous solution with a sodium bisulfite solution in an amount sufficient to provide sufficient sodium bisulfite to react with substantially all of the sodium sulfide in said aqueous solution for a total contact time of less than .1 second at a boiling temperature, whereby direct sulfitation occurs, spraying the mixed solution, and passing stripping steam through the sprayed solution, the amount of steam exceeding 40 pound moles per pound mole of sodium sulfide in said aqueous solution, whereby formation of sodium thiosulfate and associated substances is substantially avoided.

5. In a sodium base, sulfite pulping process, the improvement which comprises the steps of concentrating the spent liquor from the pulping process, burning the concentrated liquor to provide a smelt having a sulfidity of between about 45 percent and about 70 percent, the reduction of said smelt being in excess of 85 percent, dissolving said smelt to provide an aqueous solution having a sulfidity of between about 45 percent and about 70 percent and mixing said aqueous solution with a sodium bisulfite solution in an amount sufficient to provide sufficient sodium bisulfite to react with substantially all of the sodium sulfide in said aqueous solution for a total contact time of less than 5 seconds at a boiling temperature, whereby direct sulfitation occurs, spraying the mixed solution, said spray establishing a surface area at a rate in excess of 100 square feet per minute per gallon of solution sprayed, and passing stripping steam through the sprayed solution, whereby formation of sodium thiosulfate and associated substances is substantially avoided.

6. In a sodium base, sulfite pulping process, the improvement which comprises the steps of concentrating the spent liquor from the pulping process, burning the concentrated liquor to provide a smelt having a sulfidity of between about 45 percent and about 70 percent, the reduction of said smelt being in excess of 85 percent, dissolving said smelt to provide an aqueous solution having a sulfidity of between about 45 percent and about 70 percent, the concentration of sodium sulfide in said smelt solution being less than about 2.0 gram moles per liter and mixing said aqueous solution with a sodium bisulfite solution in an amount sufficient to provide sufficient sodium bisulfite to react with substantially all of the sodium sulfide in said aqueous solution for a total contact time of less than 5 seconds at a boiling temperature, whereby direct sulfitation occurs, said bisulfite solution including sodium sulfite, the molar ratio of sodium bisulfite to sodium siulfiite plus sodium bisulfite being less than .9, spraying the mixed solution, and passing stripping steam through the sprayed solution, the amount of steam exceeding 40 pound moles per pound mole of sodium sulfide in said aqueous solution, whereby formation of sodium thiosulfate and associated substances is substantially avoided.

7. In a sodium base, sulfite pulping process, the improvement which comprises the steps of concentrating the spent liquor from the pulping process, burning the concentrated liquor to provide a smelt having a sulfidity of between about 45 percent and about 70 percent, the reduction of said smelt being in excess of 85 percent, dissolving said smelt to provide an aqueous solution having a sulfidity of between about 45 percent and about 70 percent and having a pH in excess of 11.0 and mixing said aqueous solution with a sodium bisulfite solution in an amount sufficient to provide sufficient sodium bisulfite to react with substantially all of the sodium sulfide in said aqueous solution for a total contact time of less than .1 second at a boiling temperature, whereby direct sulfitation occurs, spraying the mixed solution, and passing stripping steam through the sprayed solution, the amount of steam exceeding 40 pound moles per pound mole of sodium sulfide in said aqueous solution, whereby formation of sodium thiosulfate and associated substances is substantially avoided.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,987,432 June 6, 1961

Roy P. Whitney et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 41, for "form" read -- from --; column 4, line 74, for "mask" read -- tank --; column 6, Table I, line 11 thereof, for "Reaction" read -- Reacted --; column 8, line 25, for "vent" read -- event --; column 9, line 33, for "siulfide" read -- sulfide --; column 10, line 20, for "siulfiite" read -- sulfite --.

Signed and sealed this 24th day of October 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents

USCOMM-DC