June 16, 1953 J. E. GREENAWALT 2,642,336

CONVERSION OF SODIUM SULFIDE TO SODIUM SULFITE

Filed May 26, 1948

2 Sheets-Sheet 1

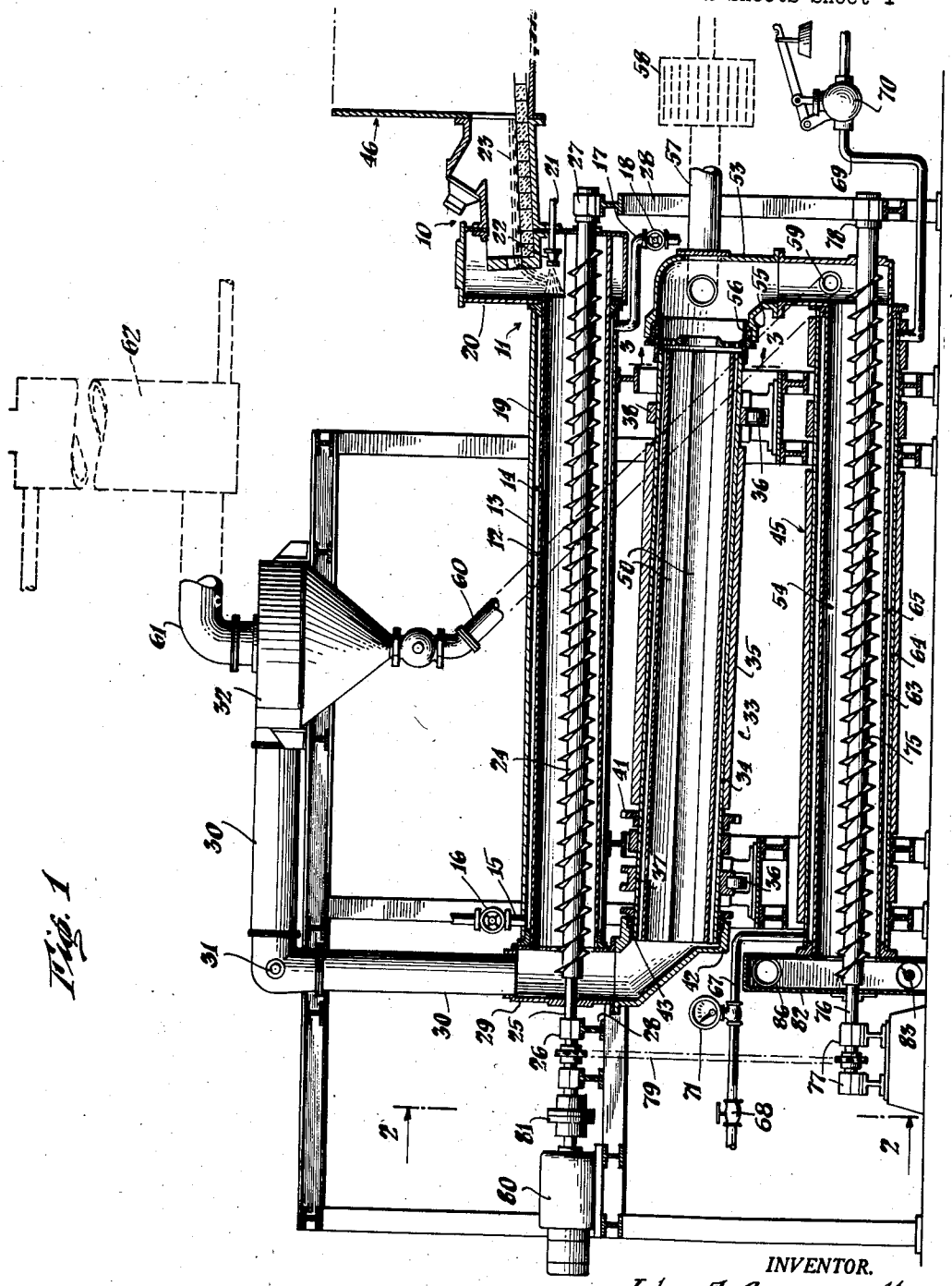

Fig. 1

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Fig. 3

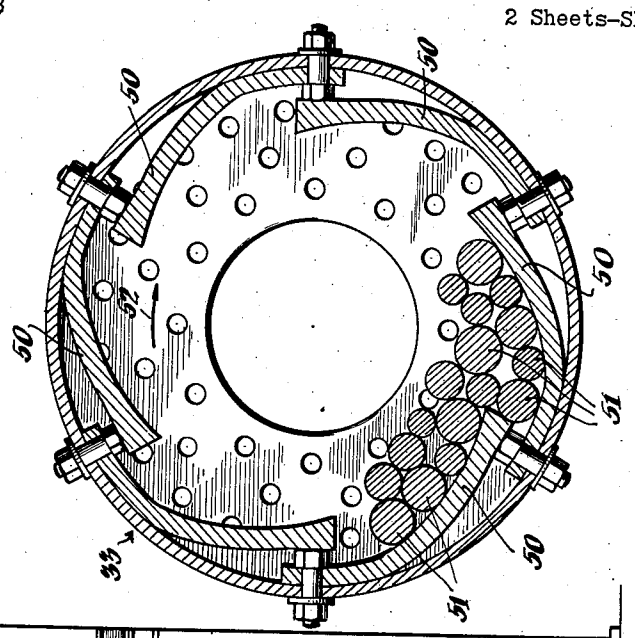
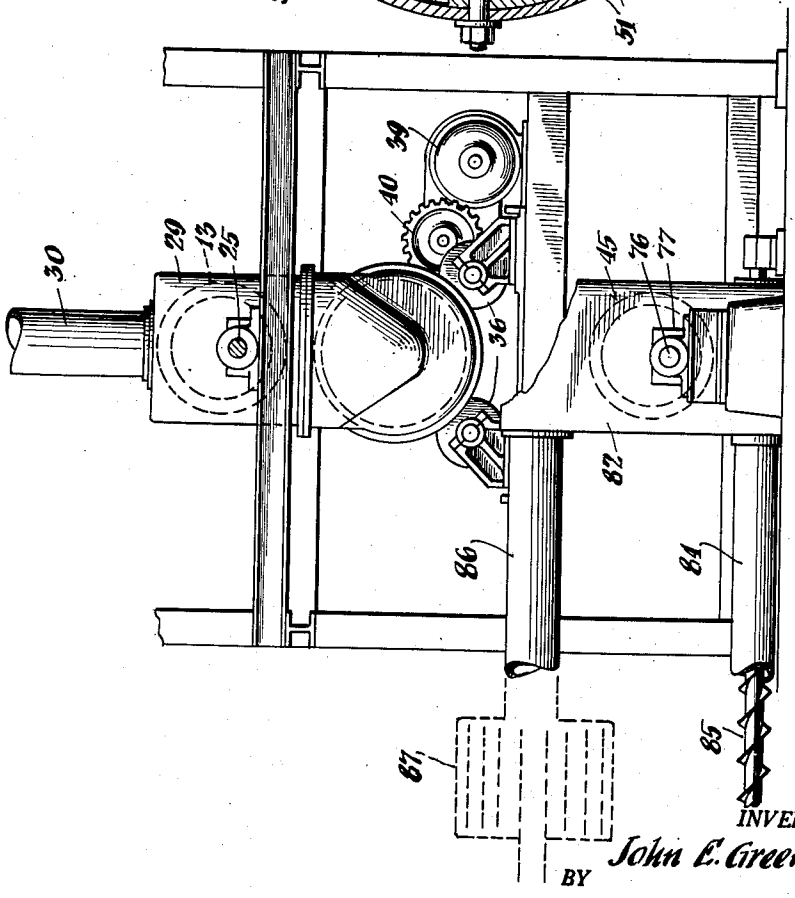


Fig. 2



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Patented June 16, 1953

2,642,336

UNITED STATES PATENT OFFICE

2,642,336

CONVERSION OF SODIUM SULFIDE TO SODIUM SULFITE

John E. Greenawalt, Bronxville, N. Y.

Application May 26, 1948, Serial No. 29,204

15 Claims. (Cl. 23—129)

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This invention relates to the production of the sulphites of alkali metals and more particularly to conversion of sodium sulphide (Na_2S) to sodium sulphite (Na_2SO_3).

Although there are many recognized uses for sodium sulphite, one that is particularly important is its use in the paper manufacturing industry. In this industry the use of a cooking or digesting liquor containing sodium sulphite or a mixture of sodium sulphite and sodium bisulphite is known and is often preferred over the use of the caustic soda process or the sulphate process in which a mixture of caustic soda and sodium sulphide are the principal ingredients in the cooking liquor. By use of the sulphite cooking liquor, a greater yield of pulp fibers having superior qualities is obtained than by the use of the other cooking liquors mentioned. This increased yield of superior quality pulp may be as much as 25% more than can be obtained by the use of either the caustic soda process or the sulphate process in which a mixture of caustic soda and sodium sulphide are the principal ingredients in the cooking liquor. This is believed to be due to the fact that sodium sulphite is much milder in its action, and it dissolves only relatively small portions of the valuable fibers or cellulose portion of the wood, yet if properly applied it is sufficiently strong to act upon the incrusting or non-cellulose portions of the wood to release the fibers that are desired in the pulp. Also, this milder action of the sodium sulphite on the wood in the digesters preserves the natural strength of the fibers to a much greater degree than the more active agents, such as caustic soda and sodium sulphide. But, whatever be the explanation, the use of sodium sulphite in the paper manufacturing industry would, I believe, be much more extensive because of the superior quality of pulp obtainable by its use but for the fact that heretofore the known processes of producing or reclaiming the sodium sulphite from the residual cooking liquor has been too inefficient or high in cost to warrant its use in many instances where it otherwise would be used.

It is, therefore, an object of my invention to provide a process of producing sodium sulphite in a more direct and efficient manner than processes that have heretofore been suggested or practised and also to provide apparatus for carrying out my improved process. Division having been required by the Patent Office, the claims of this application are directed to the process. The apparatus is claimed in applicant's copending

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application Serial No. 302,157 filed August 1, 1952, which is a division of this application.

It is, of course, known that the spent cooking liquor from the pulp digesters may be concentrated and then burned and smelted to produce sodium sulphide from the sulphur compounds present. Or sodium sulphide may be obtained from other sources. Also, it has heretofore been suggested that the sodium sulphide be converted to sodium sulphite. One method that has been suggested is the conversion of hydrous sodium sulphide to sodium sulphite, the conversion being accomplished in accordance with the following reactions:

(1) $2Na_2S+4O+H_2O=Na_2S_2O_3+2NaOH$

(2) $3Na_2S_2O_3+6NaOH=4Na_2SO_3+2Na_2S+3H_2O$

(3) $Na_2S_2O_3+2NaOH+2O=2Na_2SO_3+H_2O$

It will be seen that with such a process the conversion from sodium sulphide to sodium sulphite involves the formation of thiosulphate and then oxidizing this thiosulphate to sodium sulphite. According to the present invention sodium sulphide may be converted by direct oxidation to sodium sulphite without the intermediate formation of large amounts of the thiosulphate. The addition of water is not necessary and no caustic soda is formed or required and at all stages of the treatment only a small portion of the material is in the form of thiosulphate ($Na_2S_2O_3$). Consequently the conversion is practically all accomplished by direct oxidation of the sodium sulphide to sulphite according to the following reaction:

$$2Na_2S+3O_2\rightarrow 2Na_2SO_3$$

While my process of converting sodium sulphide to sodium sulphite is adapted for use irrespective of the source of the sodium sulphide, it is particularly well adapted for use in the paper manufacturing industry as it provides a method whereby spent sulphite cooking liquor can be reclaimed and reused in the form of sulphite cooking liquor. When wood chips, flax straw or other fiber producing material is treated with sodium sulphite, such as in the semi-chemical process, it is desirable to reclaim or recover the spent sulphite or resulting sulphur compounds in a form for reuse. Heretofore, so far as I am aware, there has been no practical and really commercially successful method of reclaiming the spent cooking liquor so that it can be reused in the form of sodium sulphite. In some instances the practice has been to waste the cooking liquor. This sometimes brings about a serious problem of stream pollution. In some in-

stances the spent liquor has been reclaimed as sodium sulphide and subsequently used in the kraft or sulphate process. But the drawback has been that there was no practical method of converting the spent liquor back to a state in which it could be used in the form of sodium sulphite. Consequently, the use of sodium sulphite in the paper and other industries has been hampered and limited, notwithstanding its many desirable and well known qualities in the manufacture of paper pulp or cellulose fiber materials. It is a further object of my invention to overcome this drawback by providing a process of reclaiming the sulphur compounds in spent cooking sulphite liquor in a form in which the sulphur compounds can be reused as sodium sulphite.

According to one way of practising my invention the spent sulphite cooking liquor resulting from the production of pulp is concentrated by evaporating off enough water to put it in a state in which it can be burned. Ordinarily the liquor is concentrated so as to contain 60% or more of solids. The concentrated liquor is then burned in a suitable furnace under reducing conditions to convert the sulphur compounds to the corresponding sulphide. In this way, sodium sulphide in dry form is produced from the spent cooking liquor. If too hot, it is first cooled and thereafter the sodium sulphide is treated in an oxidizing atmosphere, without the addition of water, to convert the sulphide to sulphite.

According to this manner of practising the process of the invention, concentrated spent sodium sulphite cooking liquor is burned in a furnace under a strong reducing atmosphere. This produces a residual molten mass of sodium sulphide and other sodium compounds, especially sodium carbonate, which can be flowed from the furnace in a very hot molten state. Heretofore, it has been common practice to drop this molten mass into a tank of water where it is dissolved to make an aqueous solution. With my process, this is not necessary. Instead, the molten mass containing sodium sulphide and sodium carbonate is retained in dry solid state and its temperature reduced. This reduction of the temperature of the molten mass should be carried out quickly. When it is sufficiently cooled it is then treated in dry state with air to oxidize the sodium sulphide to sulphite. This is done by pulverizing the mass and treating the comminuted mass in an oxidizing atmosphere. This pulverizing may be done in a ball mill, a rod mill, hammer mill, disc grinder or other machine capable of fine grinding. The oxidizing is done with air and under controlled conditions. The oxidation may, if desired, be carried out with as little as one or two percent of thiosulphate being formed while the amount of sulphite produced may be as much as 50% to 60%, the balance being substantially all sodium carbonate. A finished product may be produced in which about 90% of the sulphur compounds present is in the form of sodium sulphite.

One of the difficulties encountered in the direct oxidation of sodium sulphide is the tendency of the sulphide itself to burn or oxidize to the sulphate form, the oxidation reaction being exothermic and sodium sulphide is a highly combustible compound and may flash into flame at a low temperature. When this occurs the heat of combustion of the particles is so great that oxidation proceeds to the sulphate form. Notwithstanding the low temperature of combustion of sodium sulphide, I have demonstrated

that if the exothermic heat due to the oxidation of the sodium sulphide is controlled according to my process, the temperature of the material being treated can be as high as 250° C. without the formation of any material amount of sodium sulphate. To obtain this desirable control, I prefer to use steam under pressure in a jacket about the zone or chamber in which the material is oxidized inasmuch as a very close and fine control can be had in this manner. By adjusting the jacketed steam pressure its temperature can be correspondingly controlled. Hence, by maintaining the jacketed steam at a predetermined pressure the temperature can be maintained fixed so that the temperature of the material in the chamber, when the desired oxidation is carried out, and the temperature of the air used for the oxidation can be nicely controlled; allowance being made for the exothermic heat of oxidation of the sulphide. Although I have mentioned jacketed steam under controlled pressure, it will be understood that hot water under steam pressure may be circulated in the jacket as the water in a closed system under steam pressure may be considered as having a temperature corresponding to steam pressure.

The process may be carried out as a continuous one, the source material containing the sodium sulphide being fed, pulverized, and then progressively oxidized and continuously discharged in the sulphite form for reuse in the pulp cooking liquor or for such use as may be desired.

Although the novel features which are believed to be characteristic of the invention will be pointed out in the annexed claims, the invention itself as to its objects and advantages and the manner in which it may be carried out may be better understood by reference to the following description taken in connection with the accompanying drawings forming a part hereof, in which:

Fig. 1 is a view in elevation, partly in section, of apparatus embodying my invention;

Fig. 2 is a view on line 2—2 of Fig. 1; and

Fig. 3 is a view in cross-section, to larger scale, of the rod mill to illustrate the manner of pulverizing the material to be oxidized.

The drawings illustrate an apparatus in which my process may be carried out for converting sodium sulphide to sodium sulphite when the source material is the product recovered from the burning of concentrated residual black liquor from the pulp digesters of a paper mill. It will be understood that there are other sources of sodium sulphide and that the description here given is for purposes of illustrating one embodiment of my invention which may be used for carrying out my process when the product resulting from burning black liquor is discharged from the furnace as a molten mass containing sodium sulphide and sodium carbonate. Such a furnace and a method of burning the black liquor is disclosed in my copending application Serial No. 641,995. In that apparatus the black liquor is burned in a reducing atmosphere and the sulphur compounds of the black liquor are recovered as sodium sulphide mixed with sodium carbonate. The product of the furnace is discharged as a molten flowing mass from a discharge spout which is illustrated in the drawings forming a part of this application and designated by reference number 10; the furnace being shown conventionally by dotted lines.

Spout 10 leads into a cooling chamber 11

where the hot mass discharged from the spout is quickly cooled. This chamber 11 comprises an elongate water jacketed cylinder made of an inner wall 12 and an outer concentrically mounted wall 13 forming a jacketed space 14 through which to circulate a cooling medium, such as water. The jacket 14 is provided with an inlet pipe 15 with a control valve 16 and an outlet pipe 17 provided with a valve 18.

The inlet end of the jacketed cooling chamber 11 is provided with an intercommunicating receiving box 20 into which extends a steam jet pipe 21 provided with a nozzle 22 positioned to throw a jet of steam or water, if desired, into the stream of molten smelted product 23 flowing from the spout 10. The steam has a decided cooling effect upon the molten mass which may have a temperature as high as 1600° F., and disintegrates it as it falls into the cooling zone 19 of cooling chamber 11. Of course if water is used it will be converted to steam by the heat of the hot smelt.

The cooling chamber is also provided with a rotatable screw conveyor 24 extending throughout its length. Its shaft 25 is mounted to rotate in bearings 26 and 27 mounted on suitable frame members 28 which are structural steel members tied together to carry the weight of the apparatus. The screw conveyor 24 is rotated by means of a prime mover. As shown, the electric motor 80 is connected to the shaft by a driving coupling 81. Communicating with the interior of cooling chamber 19 at its discharge end is a discharge or receiving box 29. This box connects at its lower end with apparatus to comminute or grind the cooled sodium sulphide product which has been broken up during its passage through the cooling zone 19 of the cooling chamber 11. This box 29 serves as a transfer chamber or conduit from the cooling chamber 11 to the grinding apparatus.

Connected to the upper end of the transfer box 29 is a conduit 30 provided with an exhauster or blower 31 operated by a prime mover (not shown). The blower 31 is commonly called an induced draft fan. The conduit 30 is connected to a dust collector 32 which serves to separate particles of solid product which may be carried over from the apparatus by the air stream which is mentioned hereinafter.

The broken up particles of sodium sulphide product are delivered from the cooling chamber 19 through the transfer box 29 into the grinding apparatus which in this case is a rotatable rod mill 33. Although I prefer a rod mill, other types of comminuting or grinding apparatus, such as a ball mill, hammer mill, or disc grinder, will suggest themselves in the light of the present disclosure, it being significant to note that suitable means should be provided to finely pulverize the source material containing the sodium sulphide.

As shown the rod mill 33 comprises an elongate rotatable cylinder 34 provided with insulation 35. It is mounted to rotate about its axis on a plurality of supporting rollers 36 carried on the structural members of the frame. At the inlet end the supporting rollers 36 ride in a recessed ring track 37 secured to the cylinder 34 and at the discharge end the rollers 36 engage a ring track 38. The rod mill is driven by a prime mover. As shown, electric motor 39 (see Fig. 2) drives the pinion gear 40 which engages a ring gear 41 (see Fig. 1) fixed to the cylinder 34. It will be noted that the transfer box 29 outlet end has a collar 42 into which the cylinder 34 extends. A packing gland 43 is provided to make the connection substantially airtight.

As shown in Fig. 3 the interior of the rod mill is provided with a number of spiral shaped guide baffles 50 and free falling rods 51. Thus when the rod mill is rotated in the direction of arrow 52 the rods 51 serve to grind the broken up pieces of sodium sulphide product. And it is significant to note that as this material works its way through the rod mill to its discharge end there is a progressive pulverizing of the particles which provides for progressively exposing new surfaces of the material to the oxidizing air which, as explained hereinafter, is passed through the mill countercurrent to the passage of the charged material.

The discharge end of the rod mill is connected to a discharge box 53 which serves as a transfer chamber or conduit into the oxidizing chamber, which is designated generally by reference numeral 45. This stationary transfer box for the pulverized material has a collar 55 which extends over the end of the cylinder 34 and is provided with a packing gland 56 to maintain the connection substantially airtight. The transfer box 53 is provided with air conduit 57 for introducing air into the rod mill to oxidize the sodium sulphide as it is being progressively pulverized and as it passes through the rod mill. An air heater 58 (shown conventionally) is provided to heat the air so that it can be introduced into the grinding mill under controlled conditions of temperature. The lower end of the transfer box 53 is connected to the oxidizing chamber 54. It is also provided with an inlet 59 which is connected by a conduit 60 to the dust collector 32 so that any solid particles collected in the dust collector may be returned to the system and introduced into the oxidizing chamber 54 along with pulverized material from the rod mill 33. It may be noted here that the air stream from the dust collector 32 passes through a discharge conduit 61 through which it may be passed to a scrubber 62 (shown conventionally) to recover any fine particles of material which may escape from the dust collector. Residual air and gases can then be passed out through a stack (not shown).

The oxidizing chamber 54 is formed by an elongate cylinder 63 which is provided with a concentrically mounted cylinder 64 forming a jacketed space 65 for the circulation of a heat transfer medium such as steam or hot water. This steam jacketed oxidizing chamber 54 is further insulated by a suitable insulating material 66. Thus there is provided an oxidizing chamber with a temperature controlling jacket. An inlet pipe 67 into the jacketed space 65 is provided with a valve 68 and an outlet pipe 69 is provided with a control valve 70 so that the temperature of the oxidizing chamber can be controlled by controlling the jacket temperature, as desired. Assuming steam is being used as a heat transfer medium within the jacketed space 65, its temperature can be nicely and closely controlled by adjustment of the steam pressure as indicated by a gauge 71 connected to the steam pressure system of the plant, it being sufficient to note here that the temperature of water and steam in a steam boiler follows or is a function of the steam pressure.

The oxidizing chamber 54 is provided with a rotatable screw conveyor 75, the shaft 76 of which is mounted to rotate in suitable bearings

77 and 78 supported in the frame members. It is rotated by means of a chain drive 79 connected to the driven shaft of motor 80, which is connected by coupler 81 to shaft 25. Consequently motor 80 drives screw conveyor 24 in the cooling chamber 19 and screw conveyor 75 in the oxidizing chamber 54.

Connected to the discharge end of the oxidizing chamber is a finished product receiving box 82 which is provided with a discharge port 83. This is connected to a discharge conduit 84 provided with a screw conveyor 85 to carry the finished product to a suitable place for subsequent use. Also connected to the receiving box 82 is an air conduit 86 which is provided with an air heater 87 (shown conventionally) to heat the air so that it can be introduced into the oxidizing chamber 54 under controlled conditions of temperature and passed countercurrent to the material being oxidized. Thus it will be noted that the apparatus provides a temperature controlled oxidizing chamber through which pulverized sodium sulphide or other pulverized material containing sodium sulphide may be passed and into which air under controlled conditions can be introduced and passed countercurrent to the pulverized material. It will be seen also that there is provided means for pulverizing the source material and means for cooling the source material prior to comminution, all in a substantially closed system under controlled conditions of temperature.

To illustrate my process for converting sodium sulphide to sodium sulphite, it may be described in connection with the accompanying drawings as applied to the smelt from the concentrated cooking liquor from the semi-chemical process or from the cooking liquor produced in the sodium sulphite process in which the predominating ingredient in the original cooking liquor is sodium sulphite. In either case, the residual cooking liquor is concentrated, and burned in a reducing atmosphere. This produces a smelt containing the sulphur compounds in the form of sodium sulphide along with sodium carbonate. The smelt is produced in molten state which may be flowed from the furnace (shown conventionally at 46) through a discharge spout 10, some of the reducing gases from the furnace 46 being drawn along through the spout.

The hot molten smelt 23 containing sodium sulphide drops from the furnace spout 10 into receiving box 20 where it encounters steam from the nozzle of jet 21. Here the smelt is broken up, partly solidified and partially cooled as it is blown by the steam into the cooling chamber 19. The charge is conveyed through this chamber and further broken up by the screw conveyor 24. If a more intensified cooling of the molten stream is desired, water or a mixture of water and steam may be jetted into the molten smelt through jet 21. While the charge of material is passing through the chamber 19 it is subjected to the cooling action of the water cooled walls of this chamber; the jacket 14 being cooled by circulating water.

Since the sodium sulphide is highly combustible at high temperatures, it is protected until cooled to about 150° C. by non-oxidizing gases drawn from the furnace by the exhaust fan 31. Cooling water to control the temperature of the cooling chamber is introduced through pipe 15, passes through jacket 14, and is discharged through pipe 17.

The solid partially cooled charge from cooling chamber 19 is discharged into transfer box 29 and thence into rod mill 33 where the material is crushed and progressively finely pulverized. While a rod mill is shown, the pulverizing step can be effected in any one of numerous machines designed for pulverizing, but I consider a rod mill preferable as considerable of the oxidizing of the sodium sulphide can be accomplished simultaneously with the crushing. And, in this manner, the speed of oxidation can be reduced largely to the action on the surface of the particles since the oxidation does not readily penetrate the surface of the particles, thus making it very difficult to oxidize the interior of these solid particles. By continuously crushing the particles, new surfaces are continuously exposed to the oxidizing action of the air current as the material slowly works its way through the rod mill. Air in desired amount and temperature is introduced through conduit 57 and flows through the rod mill countercurrent to the material. By the time it reaches the fresh material coming from the cooler 19 it is denuded of considerable oxygen and this further reduces the intensity of the oxidizing action when the material is richer in sodium sulphide. I have found that it is the too rapid oxidation of sodium sulphide particles that increases the temperature of the particles beyond that of the predetermined temperature of the oxidizing apparatus and it is this increased temperature which should be avoided because otherwise the oxidation will proceed to form unwanted sulphate.

When the temperature of the particles reaches about 250° C. the tendency to form sulphate is noticeable and the higher the temperature the greater is the tendency to form sulphate. An important thing is to control the temperature of the particles undergoing oxidation and this may be done in my apparatus. This is accomplished by using steam as a heat transfer medium and controlling the temperature of the steam by its pressure, while at the same time constantly agitating and disturbing the particles with relation to each other while they are undergoing the oxidizing process so as to disperse the heat created by the oxidation of the sulphide particles. This control of temperature and the other conditions is done by controlling the conditions of oxidation in the oxidation chamber 54.

As the partially oxidized pulverized material is discharged from the rod mill 33 it passes through transfer box 53 into the oxidation chamber 54. It is moved through this chamber by the screw conveyor 75, which keeps the finely ground particles agitated. The temperature in the chamber is controlled by controlling the temperature of the steam passing through the jacket 65. The steam temperature is controlled by controlling its pressure. That is, it is possible to maintain the desired temperature in the oxidizing chamber by maintaining a predetermined steam pressure, the temperature being varied as desired by varying the steam pressure. I have obtained excellent results in an oxidizing chamber of this sort with a boiler pressure of 200 pounds (lbs. per square inch) which maintained a temperature about 220° C. in the oxidizing chamber. The temperature of the air introduced into this chamber through conduit 86 should be at about 180° C. The temperature of the air can be maintained by passing it through the air heater 87 which is heated with steam from the plant boiler. The oxidizing action may, in some instances, be improved by mixing

a small amount of steam with the air. The action of the rotating screw conveyor **75** slowly advances the material through the chamber **54** and at the same time continuously exposes new surfaces of the material to the oxidizing action of the heated air current passing countercurrent to the material. The temperature of the mass of pulverized particles undergoing oxidation should not substantially exceed 250° C. and should not be below about 160° C. For best results according to my present experience, the temperature in the mass of particles in the oxidizing chamber should be at about 220° C.

The steam for maintaining the desired temperature within the oxidizing chamber **54** enters the jacket **64** through the pipe **67** and passes out of the jacket with such water as may condense. The air passes through the chamber **54**, then passes through the box **53**, thence through the crushing chamber or rod mill **33** to the induced draft fan **31**, which blows the residual products of combustion and fine particles which may float in it, into the dust collector **32**. Particles collected in the dust collector are returned through conduit **60** to the mainstream in box **53** for recovery. Residual air and gases from the dust collector are led to the scrubber **62** and finally to the stack. The induced draft fan **31** also withdraws reducing gases from the furnace through the spout **10**, through the cooling chamber **19**, and discharges these products along with the gas stream to the collector **32** along with such residual air as results from the introduction of air through conduits **83** and **57**. The treated or finished material is discharged from the oxidizing chamber **54** into box **82** and thence through discharge conduit **84**. The recovered material contains sodium sulphite which was initially present in the charge as sodium sulphide and also sodium carbonate which was initially present. The recovered product may then be dissolved in water and filtered to make up sulphite cooking liquor for the pulp digesters. After use in the digesters, the residual cooking liquor may then be recycled as described above, it being significant to note that there is no undue accumulation of sodium sulphate from recycling because sodium sulphate is reduced to sulphide in the reducing furnace.

Although the smelt coming from the furnace which makes up the charge contains other compounds besides sodium sulphide, such as sodium carbonate and possibly some carbon, these are not harmful to my process. In fact there is an advantage because they dilute the charge so that it is not so rich in sulphide and this aids in the prevention of local heat of combustion or oxidation from forming too rapidly. The carbon, if present, is also helpful in the pulverizing step because the sodium sulphide will oxidize at a temperature below the ignition point of carbon, so that both the carbon and sodium carbonate present pass through the process unaffected.

When my process is used as a cyclic process, the recovery of chemicals will be very high, running from 90% to 95%, but of course some losses will occur in the wash water and other losses due to leaks and loss through furnace gases will occur. These small losses must be replenished but this may be done very economically according to my process by adding salt cake, or sodium sulphate, to the reducing furnace charge where it is reduced to sodium sulphide and the sodium sulphide then converted to sodium sulphite by my oxidizing process. If it is desired to further enrich the smelt from the reducing furnace so that it will contain more sodium sulphide, this may be done by adding the desired amount of sodium sulphate to the reducing furnace. The added sodium sulphate, which may be in the form of salt cake, is reduced to sodium sulphide and discharged as such along with the smelt from the furnace.

The following examples are given further to illustrate the process of my invention.

EXAMPLE I

According to one example of practising the process of my invention, a charge containing 35% of commercial sodium carbonate and 65% sodium sulphide in molten state was cooled by subjecting it to a jet of steam in a cooling chamber, the material was then crushed and passed through an oxidizing chamber into which a heated air current was passed, the temperature of the mass undergoing oxidation being maintained at about 220° C. The resulting treated material contained 71% sodium sulphite (Na_2SO_3), 5% sodium sulphide (Na_2S), 1% sodium thiosulphate ($Na_2S_2O_3$), 3% sodium sulphate (Na_2SO_4), the balance being sodium carbonate. Accordingly approximately 68% of the sodium sulphide was converted to sulphite with very little formation of thiosulphate and sulphate. In the light of later experience it was found that crushing the material to greater fineness resulted in substantially higher yields of sulphite.

EXAMPLE II

In another example, a charge of molten smelt was drawn from the spout of a reducing furnace such as illustrated in the drawings. This smelt resulted from the burning of a concentrated black liquor from the digester of a paper mill. This smelt, herein called the charge, consisted of sodium carbonate, sodium sulphide, and a small amount of sodium sulphate. It was then treated to convert the sodium sulphide to sodium sulphite. The charge was quickly cooled in a cooling chamber to about 150° C. It was then ground in a disc grinder, through which air was passed. The material discharged from the disc grinder had a fineness analysis approximately as follows:

Screen analysis

	Per cent
Retained on 100 mesh screen	4.73
Retained on 150 mesh screen	1.71
Retained on 200 mesh screen	5.33
Retained on 300 mesh screen	53.65
Passed by 300 mesh screen	34.58
Total	100.00

The crushed material was then passed through the oxidizing chamber countercurrent to the preheated oxidizing air which was introduced into the oxidizing chamber. The temperature of the oxidizing chamber was controlled so that the mass of pulverized charge was about 220° C. The treated or finished product discharged from the oxidizing chamber analyzed approximately as follows:

	Per cent
Insoluble	2
Sodium sulphite (Na_2SO_3)	47
Sodium thiosulphate ($Na_2S_2O_3$)	2
Sodium sulphide (Na_2S)	4
Sodium sulphate (Na_2SO_4)	4
Sodium carbonate (Na_2CO_3)	43

Thus it will be seen that my process is admirably suited to converting the sulphur compounds in spent liquor from the pulp digester into sodium sulphite for making up sodium sulphite cooking liquor for use or reuse in the pulp digesters.

EXAMPLE III

In another instance a charge was treated to convert its sodium sulphide to sodium sulphite. This charge was the smelt from a reducing furnace wherein waste black liquor from a pulp digester was burned. The molten charge was quickly cooled by a steam jet and passed through a cooling chamber to prevent oxidation until it had a temperature of about 150° C. The charge was ground to a fineness of the order mentioned in Example II. It was then passed through a steam jacketed oxidizing chamber through which preheated air was passed countercurrent to the ground charge. The temperature in the oxidizing chamber was maintained at about 220° C. by controlling the pressure of the steam in the jacket around the oxidizing chamber.

The finished product was analyzed and found to be as follows:

	Per cent
Insoluble	1
Sodium sulphite (Na_2SO_3)	27
Sodium thiosulphate ($Na_2S_2O_3$)	2
Sodium sulphide (Na_2S)	1
Sodium sulphate (Na_2SO_4)	3
Sodium carbonate (Na_2CO_3)	63

It will be observed that of the sulphur compounds in the finished product most of it is in the form of sodium sulphite, there being only 1% of sulphide left unconverted and only 2% and 3% respectively of thiosulphate and sulphate was present, the amount of sodium sulphite being more than 80% of the sulphur compounds present.

From the foregoing disclosure it will be noted that my invention is characterized by a number of important and commercially advantageous features. It provides a process by which sodium sulphide can be converted to sodium sulphite by pulverizing solid sodium sulphide or a source material containing sodium sulphide and subjecting the pulverized particles to an oxidizing atmosphere at a temperature below that at which sodium sulphate would form in undue amount. The process may be carried out by direct oxidation of Na_2S to Na_2SO_3 without formation of undue amounts of sodium thiosulphate in the finished product or as an intermediate reaction product. It provides a process by which larger particles may be progressively reduced in size to expose new surfaces progressively to the oxidation medium and thus better control of the temperature conditions with prevention of flashing with its attendant generation of exothermic heat sufficient to raise the temperature of the mass to a point where sulphate is formed. The process may be carried out as a continuous one and it will be noted it may be carried out advantageously by a progressive and controlled oxidation process wherein the material richest in sodium sulphide is progressively converted to a material richer in sodium sulphite by passing the oxidizing air in countercurrent flow whereby the air becomes progressively poorer in oxygen and the material under treatment becomes progressively richer in sodium sulphite.

Not only is my process adapted for use in converting sodium sulphide from various sources to sodium sulphite but it is particularly suited to a cyclic process in the paper manufacturing industry where it is desired to use the sodium sulphite process because the sulphur compounds in the spent liquor can be reconverted to sulphite form for reuse over and over again.

Moreover, a novel apparatus is provided for carrying out the process wherein the cooling, grinding and oxidation may be carried out as a continuous process under controlled conditions, it being particularly significant to note that the temperature of the mass of charge can be positively and nicely controlled by the use of a predetermined steam pressure. This is particularly useful in a commercial plant because the plant steam boilers may conveniently, economically and advantageously be used in a simple manner to serve as a means for controlling the temperature in the oxidation process.

The terms and expressions which have been employed herein are used as terms of description and not of limitation and there is no intention in the use of such terms and expressions of excluding any equivalent of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of invention claimed.

What I claim is:

1. A process of treating a charge containing sodium sulphide to convert the sodium sulphide to sodium sulphite which comprises passing said charge in dry state through a pulverizing chamber, passing air through said chamber in contact with said charge, maintaining said charge dry and progressively pulverizing and continuously agitating said charge in said chamber thereby to expose fresh surfaces of sodium sulphide to the oxidizing action of said air while controlling the temperature in said pulverizing chamber within predetermined limits, thereafter passing the pulverized dry particles of charge being treated through another chamber and continuously agitating said particles while passing air therethrough in intimate contact with said dry pulverized charge, and maintaining the temperature in said other chamber at a temperature sufficiently high to oxidize the sodium sulphide to sodium sulphite but not high enough to form more than small amounts of sodium sulphate, thereby to convert the sodium sulphide to sodium sulphite.

2. A process of treating a charge containing sodium sulphide to convert the sodium sulphide to sodium sulphite which comprises passing said charge in dry state through a pulverizing chamber, passing air through said chamber in contact with said charge, progressively pulverizing said charge in said chamber thereby to expose fresh surfaces of sodium sulphide to the oxidizing action of said air while controlling the temperature in said pulverizing chamber within predetermined limits, thereafter passing the dry pulverized charge being treated through another chamber while passing air therethrough in intimate contact with said dry pulverized charge, and controlling the temperature in said other chamber at a temperature sufficiently high to oxidize the sodium sulphide to sodium sulphite but not high enough to form more than small amounts of sodium sulphate, thereby to convert the sodium sulphide to sodium sulphite, said temperature control being effected by the use of steam the temperature of which is adjusted by adjustment of its pressure.

3. A process of treating a charge containing

sodium sulphide to convert the sodium sulphide to sodium sulphite which comprises passing said charge in dry state through a pulverizing chamber, passing air through said chamber in contact with said charge, progressively pulverizing said charge in said chamber thereby to expose fresh surfaces of dry sodium sulphide to the oxidizing action of said air while controlling the temperature in said pulverizing chamber within predetermined limits, thereafter passing the dry pulverized charge being treated through a jacketed chamber while passing air through said jacketed chamber in intimate contact with said dry pulverized charge, and maintaining the temperature in said jacketed chamber at a temperature sufficiently high to oxidize the sodium sulphide to sodium sulphite but not high enough to form more than small amounts of sodium sulphate, thereby to convert the sodium sulphide to sodium sulphite, the temperature in said jacketed chamber being effected by passing steam under controlled pressure through the jacket.

4. A method of treating the sodium sulphide contained in the smelt from a furnace wherein sulphur compounds are converted to sodium sulphide and the smelt from the furnace is discharged as a molten mass containing sodium sulphide and other sodium compounds including sodium carbonate which method comprises cooling the molten smelt discharged from the furnace to a temperature at which it solidifies, thereafter pulverizing the solidified product in dry state, and subjecting the dry pulverized product to an oxidizing atmosphere while progressively exposing new surfaces of the dry pulverized product to the oxidizing atmosphere at a temperature sufficiently high to oxidize the sodium sulphide to sodium sulphite but not higher than that at which the sodium sulphide would be oxidized to sodium sulphate in more than negligible amounts.

5. A method of treating the sodium sulphide contained in the smelt from a furnace wherein sulphur compounds are converted to sodium sulphide and the smelt from the furnace is discharged as a molten mass containing sodium sulphide and other sodium compounds including sodium carbonate which method comprises cooling the molten smelt discharged from the furnace to a point where it solidifies by contacting the molten smelt with a jet of aqueous cooling medium, thereafter pulverizing the solidified product in dry state in a pulverizing chamber through which air is passed in contact with the product to be pulverized while progressively exposing new surfaces of the dry pulverized product to the oxidizing action of the air at a temperature sufficiently high to oxidize the sodium sulphide to sodium sulphite but not higher than that at which the sodium sulphide would be oxidized to sodium sulphate in more than negligible amounts, thereafter passing the pulverized particles through an oxidizing chamber through which air is passed in intimate contact with said particles while maintaining the temperature within said oxidizing chamber at a temperature sufficiently high to oxidize the sodium sulphide but not higher than that at which the sodium sulphide would be oxidized to sodium sulphate in more than negligible amounts, thereby to convert substantially all of the sodium sulphide contained in said smelt to sodium sulphite.

6. A continuous process of converting the sodium sulphide contained in a charge to sodium sulphite by oxidizing the sodium sulphide to sodium sulphite with oxygen from air which comprises continuously introducing the charge in dry state in a grinding chamber where the charge while in dry state is progressively pulverized dry, passing the pulverized charge from the grinding chamber through an oxidizing zone from which it is discharged, continuously introducing a current of air into said oxidizing zone in which the temperature is controlled within limits to effect oxidation of the sodium sulphide without formation of substantial amounts of sodium sulphate, said air current passing through said oxidizing chamber and pulverizing chamber in intimate contact with the charge and countercurrent to the passage of the charge and becoming progressively poorer in oxygen content while the charge introduced into said grinding chamber and discharged from said oxidizing chamber becomes progressively poorer in sodium sulphide and richer in sodium sulphite.

7. A method of converting sodium sulphide contained in a pulverized charge of material containing the sodium sulphide which comprises continuously passing the pulverized charge in dry state through a chamber and passing a stream of air through said chamber countercurrent to the passage of said charge while agitating the particles of pulverized charge in intimate contact with said moving stream of air, the method being carried out as a continuous process wherein the pulverized charge as it passes through said chamber is maintained under conditions effective to convert sodium sulphide to sodium sulphite and the stream of air becomes progressively poorer in oxygen content and the charge becomes progressively richer in sodium sulphite and progressively poorer in sodium sulphide.

8. A method of producing sodium sulphite suitable for use in cooking liquor in the digesters of a paper mill which comprises recovering the sulphur compounds as sodium sulphide from spent cooking liquor as a smelt from a reducing furnace, adding sodium sulphate to the furnace to increase the content of sodium sulphide in the smelt drawn from the furnace, cooling the smelt while maintaining it under condition to keep it dry; then pulverizing the dry smelt containing the sodium sulphide and subjecting the dry pulverized smelt to an oxidizing atmosphere under dry conditions effective to convert the sodium sulphide in the dry smelt to sodium sulphite.

9. A process of converting sodium sulphide to sodium sulphite in a charge in solidified form containing other sodium compounds which comprises pulverizing said charge which contains said sodium sulphide by grinding the solidified charge in dry form, passing the pulverized dry charge through a reaction zone and simultaneously passing a current of air through said reaction zone in intimate contact with the pulverized charge and in sufficient amount to oxidize said sodium sulphide to sodium sulphite, agitating said pulverized charge while in said reaction zone thereby to cause said intimate contact between said current of air and the pulverized particles of said charge in said reaction zone, controlling the temperature in said reaction zone at a temperature sufficiently high to oxidize said sodium sulphide to sodium sulphite but below 250° C. thereby producing a pulverized product containing sodium sulphite converted from said sodium sulphide.

10. A process of converting sodium sulphide to

sodium sulphite which comprises providing a solidified charge containing sodium sulphide and other sodium compounds in dry form, grinding said solidified charge to produce pulverized dry particles without previous addition of water, passing the dry pulverized charge through a reaction zone while simultaneously passing a current of air through said reaction zone in intimate contact with the pulverized charge and in sufficient amount to oxidize said sodium sulphide to sodium sulphite, agitating said dry pulverized charge in said reaction zone thereby to cause said intimate contact between said current of air and the pulverized particles of said charge in said reaction zone, controlling the temperature of the reaction zone within the range of 160° C. and 250° C. thereby producing a product containing sodium sulphite converted from the sodium sulphide initially present in the charge and containing, if any, no more than negligible quantities of sodium thiosulphate and sodium sulphate.

11. A process of producing sodium sulphite from a dry charge containing sodium sulphide by converting the sodium sulphide to sodium sulphite without addition of water to the charge which comprises establishing a reaction zone, grinding the charge in dry condition within said reaction zone to form dry pulverized particles containing the sodium sulphide, passing the pulverized particles through said reaction zone while simultaneously passing a current of air through said reaction zone sufficient in amount to oxidize the sodium sulphide in the charge to sodium sulphite, controlling the temperature in said reaction zone within the range of 160° C. to 250° C. while causing intimate contact between said particles and said air, thereby converting said sodium sulphide to sodium sulphite.

12. A process of converting sodium sulphide to sodium sulphite which comprises pulverizing a dry charge containing said sodium sulphide to an extent that more than 30% of the pulverulent charge passes a 300 mesh screen and more than 85% passes a 200 mesh screen, passing said pulverulent charge through an oxidizing chamber and simultaneously passing an oxidizing gas in intimate contact with the pulverulent charge in said oxidizing chamber, maintaining the temperature in said chamber above 160° C. but not substantially higher than 250° C. and agitating the particles of the charge while in said chamber whereby to expose fresh surfaces of the particles containing the sodium sulphide to the action of the said oxidizing gas thereby to produce sodium sulphite by direct oxidation of the sodium sulphide.

13. A process of converting sodium sulphide to sodium sulphite which comprises passing a dry charge containing sodium sulphide in the form of pulverized particles through an oxidizing chamber, simultaneously passing a current of air through said chamber in intimate contact with said particles while maintaining the temperature within said chamber between 160° C. and 250° C., and agitating the particles in said chamber whereby to continuously subject them to the oxidizing action of said air, the temperature in said chamber being controlled by a steam heated medium out of contact with said particles, the temperature of the steam heated medium being controlled by adjusting the pressure of the steam.

14. A process of treating a fused charge containing sodium sulphide to convert the sodium sulphide to sodium sulphite which comprises pulverizing said charge in dry state, subjecting the particles of the pulverized charge in an oxidizing chamber in dry state to a current of air while maintaining the temperature of the charge in said chamber at about 220° C. and agitating the pulverized particles of the charge in said chamber whereby to expose fresh surfaces of the particles containing sodium sulphide to the oxidizing action of the air thereby to produce sodium sulphite by direct oxidation of the sodium sulphide.

15. A method of treating a charge consisting of fused pieces containing sodium sulphide to convert the sodium sulphide to sodium sulphite which comprises passing the solidified pieces into a pulverizing chamber, progressively pulverizing the charge containing sodium sulphide in dry state in said pulverizing chamber, passing air through said chamber in intimate contact with said dry charge while maintaining the temperature of the charge above 160° C. but below 250° C. thereby to oxidize the sodium sulphide to sodium sulphite without forming more than small amounts of sodium sulphate, the particles of charge being kept dry and being continuously agitated during the pulverizing of the charge whereby fresh surfaces of sodium sulphide are continuously exposed to the oxidizing action of said air during the pulverizing of the charge.

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