Sept. 13, 1955

J. E. GREENAWALT

2,717,825

APPARATUS FOR CONVERSION OF SODIUM SULPHIDE TO SODIUM SULPHITE

Original Filed May 26, 1948

2 Sheets-Sheet 1

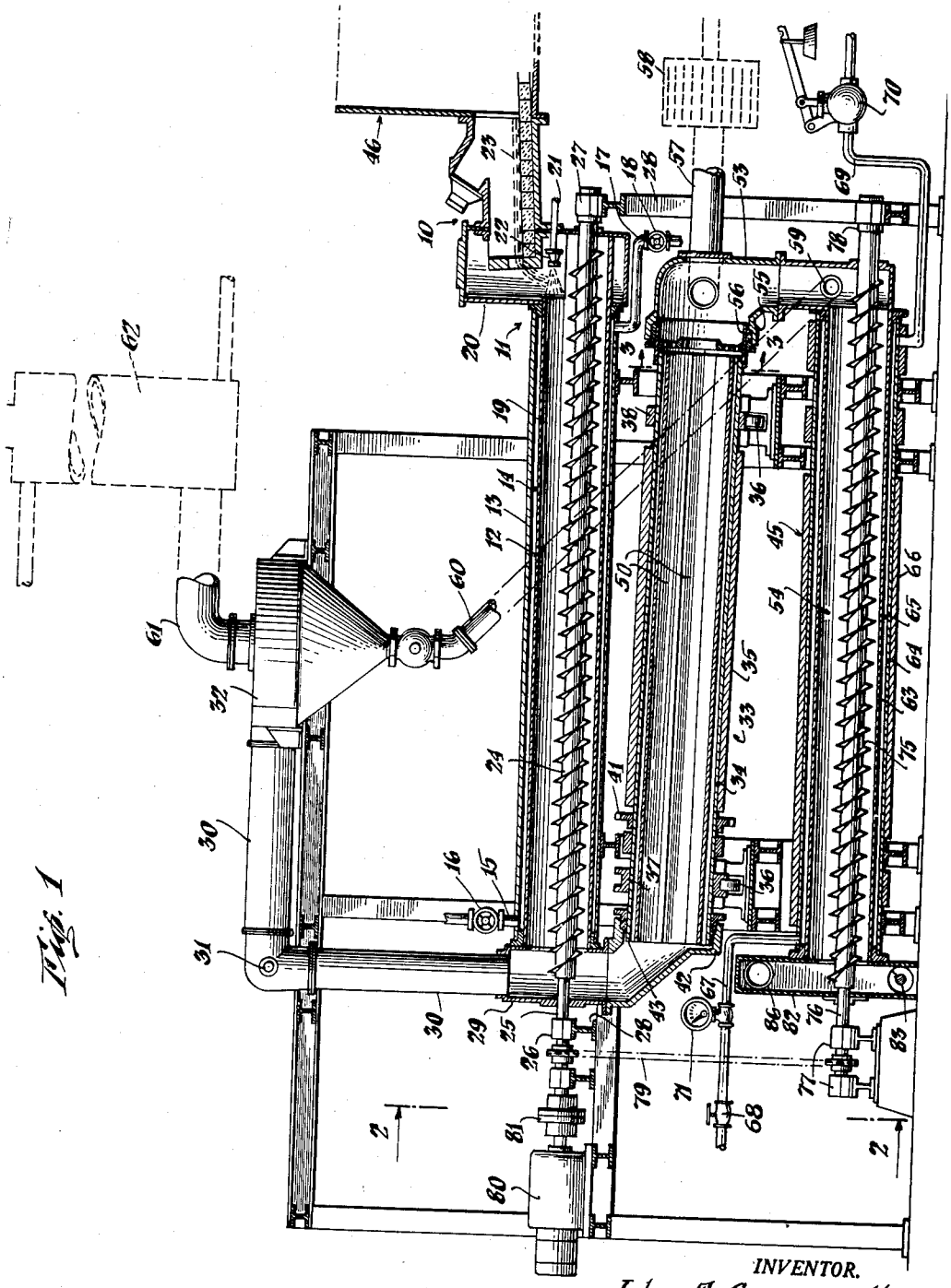


Fig. 1

INVENTOR.

John E. Greenawalt

BY

Clarence O'Kerr

ATTORNEY

Sept. 13, 1955

J. E. GREENAWALT

APPARATUS FOR CONVERSION OF SODIUM SULPHIDE TO SODIUM SULPHITE

2,717,825

Original Filed May 26, 1948

2 Sheets-Sheet 2

Fig. 3

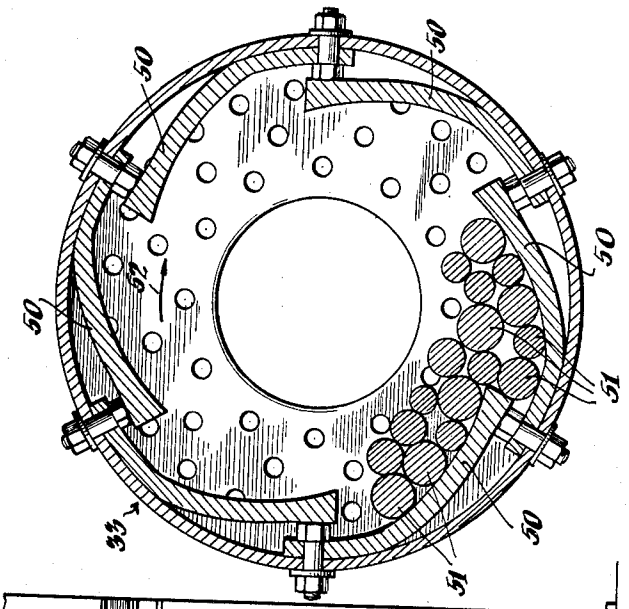
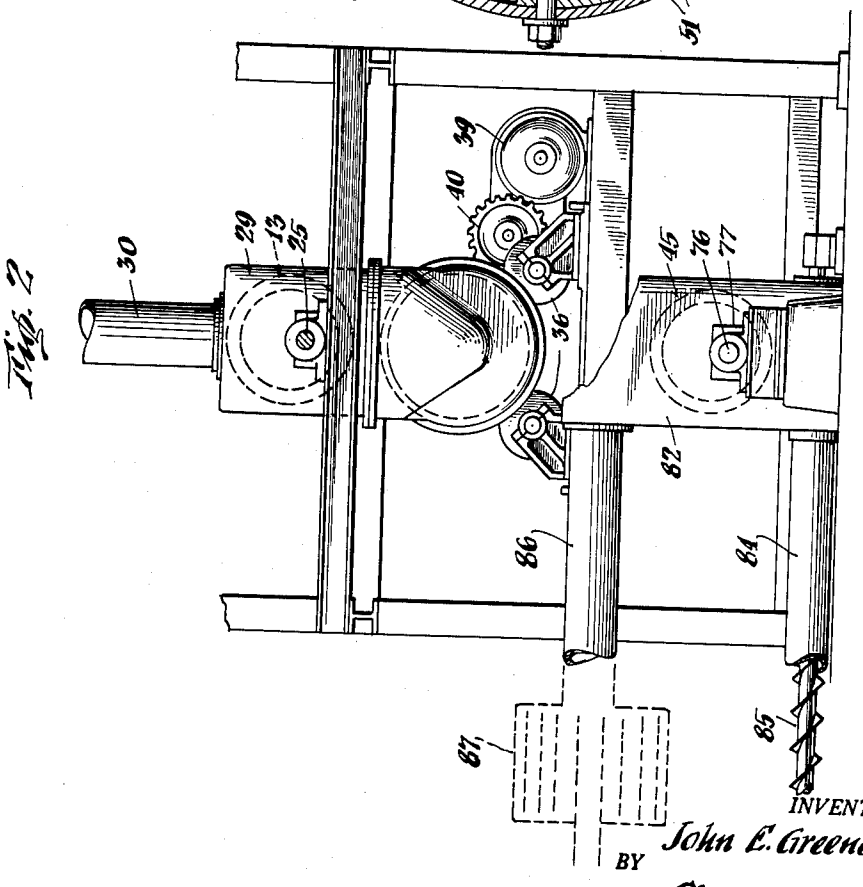


Fig. 2



INVENTOR.

John E. Greenawalt

BY

Clarence A. Kerr

ATTORNEY

United States Patent Office 2,717,825 Patented Sept. 13, 1955

2,717,825

APPARATUS FOR CONVERSION OF SODIUM SULPHIDE TO SODIUM SULPHITE

John E. Greenawalt, Bronxville, N. Y.

Original application May 26, 1948, Serial No. 29,204. Divided and this application August 1, 1952, Serial No. 302,157

5 Claims. (Cl. 23—262)

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).

This application is a division of my copending application S. N. 29,204, filed May 26, 1948, now Patent No. 2,642,336, in which the process of my invention is claimed, the claims of this application being directed to apparatus.

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 of 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 codium 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, said method being claimed in my said copending application S. N. 29,204 and said apparatus being claimed in 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 instances 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 of 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 rotata-

ble 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 in 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 225° 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. This 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 the 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 main stream 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 beside 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 sulphite 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 (NaS_2), 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 sulphite (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 at 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 sulphite (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 a 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 is claimed is:

1. Apparatus for converting sodium sulphide contained comprises an elongated jacketed cooling chamber in which the molten charge is solidified and cooled, means for introducing the molten smelt into said cooling chamber, screw conveyor means in said cooling chamber op- in a charge of molten smelt to sodium sulphite which erative to break the solidified charge into pieces and discharge them therefrom, a mill providing a chamber into which the solidified pieces containing sodium sulphide are introduced and ground to progressively pulverize them, an oxidizing chamber providing an oxidizing zone into which said pulverized product is charged, a jacket around said oxidizing chamber through which steam may be passed to control the temperature in said zone, means including an air conduit communicating with said zone for introducing air into said zone, and a conveyor means within said oxidizing chamber to move said pulverized particles therethrough to stir the particles so that fresh surfaces of the pulverized particles are continuously brought into intimate contact with air introduced into said zone, conduit means for carrying spent air from said chambers, a dust collector connected to said last mentioned conduit for collecting entrained particles of charge carried in said spent air, another conduit connecting said dust collector and oxidizing chamber for charging the collected particles to said oxidizing chamber.

2. Apparatus for producing sodium sulphite from the smelt discharged from a furnace in molten state which smelt contains sodium sulphide and sodium carbonate

which apparatus comprises a pouring spout through which to flow the molten charge of smelt into contact with a jet of steam, a jet mounted adjacent the discharge end of said spout for blowing steam into the flowing molten smelt to cool and solidify the smelt, an elongate cooling chamber the head end of which communicates with said spout into which said smelt is introduced and further cooled, conveyor means within said cooling chamber operative to break up said solidified smelt and move it through said cooling chamber, a jacket surrounding said cooling chamber through which a cooling medium is passed, means to control the flow of cooling medium through said jacket, a pulverizing chamber communicating with said cooling chamber into which the charge is passed and pulverised, a temperature controlled oxidising chamber communicating with said pulverizing chamber into which the pulverized charge is passed, a steam jacket surrounding said oxidizing chamber through which steam flows under pressure, means to regulate the pressure of the steam in said steam jacket for controlling the temperature in said oxidizing chamber, conveyor means within said oxidizing chamber operative to agitate this pulverized charge and move it through said oxidizing chamber, and means for introducing air into said oxidizing chamber and passing it thence through said pulverizing chamber countercurrent to the passing of the charge.

3. Apparatus for treating a molten charge containing sodium sulphide and sodium carbonate such as the smelt from a reducing furnace to convert the sodium sulphide to sodium sulphite which apparatus comprises an elongate jacketed cooling chamber in which to cool a charge of hot smelt, a pouring spout communicating with said cooling chamber through which to introduce smelt in molten condition into said cooling chamber, a steam jet mounted in said cooling chamber for introducing steam into said cooling chamber, conveyor means within said cooling chamber operative to move said charge therethrough and to break the charge into small pieces, a grinding mill having a pulverizing chamber the head end of which communicates with the discharge end of said cooling chamber, said grinding mill having means operative to progressively pulverize said pieces and discharge the pulverized charge therefrom, an elongate jacketed oxidizing chamber to receive the pulverized charge, the head end of which is connected to said pulverizing chamber and having a discharge end, conveyor means within said oxidizing chamber operative to move the pulverized charge discharged from said pulverizing chamber through said oxidizing chamber and discharge it therefrom, and means including a conduit for passing air into said oxidizing chamber and thence through said grinding mill chamber to oxidize the sodium sulphide in said charge to sodium sulphite.

4. Apparatus for producing sodium sulphite from the smelt from a furnace which smelt contains sodium sulphide and sodium carbonate which apparatus comprises a spout through which to flow molten smelt into contact with a jet of steam, a jet mounted adjacent the discharge end of said spout for blowing steam into the flowing molten smelt to cool and solidify the smelt, a cooling chamber communicating with said spout into which said smelt is introduced and further cooled, conveyor means in said cooling chamber operative to break the cooled smelt into small pieces and discharge them from the cooling chamber, a pulverizing chamber communicating with said cooling chamber into which the charge is passed and pulverized, grinding means in said pulverizing chamber operative to progressively pulverize said pieces, a temperature controlled oxidizing chamber communicating with said pulverizing chamber into which the pulverised charge is passed, and means for introducing and passing a stream of air into said oxidizing chamber and thence through said pulverising chamber counter-current to the passage of the charge, a dust collector, a conduit connecting said dust collector with said cooling chamber and said pulverising chamber through which said stream of air passes to said dust collector after it passes through said pulverising chamber, said dust collector serving to collect particles of the charge carried away from said cooling and pulverizing chambers in said stream of air and a conduit connecting said dust collector with said oxidizing chamber for charging the particles collected in the dust collector to said oxidizing chamber.

5. Apparatus for treating a charge containing sodium sulphide and sodium carbonate such as the molten smelt from a reducing furnace whereby to convert the sodium sulphide to sodium sulphite which apparatus comprises an elongate cooling chamber in which to cool and solidify the molten charge of hot smelt, a jacket around said cooling chamber through which to pass a cooling fluid, means to regulate the flow of said fluid for regulating the temperature in said cooling chamber, a screw conveyor within said cooling chamber operative to move said charge therethrough while it is being cooled, a grinding mill having a pulverizing chamber the head end of which is connected to the discharge end of said cooling chamber, said grinding mill having means operative to progressively pulverize said charge and discharge it therefrom, an elongate oxidizing chamber to receive the pulverized charge, the head end of which is connected to the discharge end of said pulverizing chamber and having a discharge end, a jacketaround said oxidizing chamber through which to pass a heated heat transfer medium, means to control the temperature of said medium, a screw conveyor within said oxidizing chamber operative to move the pulverized charge therethrough and discharge it therefrom, means including conduits for passing a stream of air into said oxidizing chamber and thence through said pulverizing chamber to oxidize the sodium sulphide in said charge to sodium sulphite, a dust collector communicating with said pulverizing chamber for collecting particles of charge carried by said stream of air discharged from said pulverizing chamber, and means including a conduit communicating with said oxidizing chamber for charging the collected particles into said oxidizing chamber.

References Cited in the file of this patent

UNITED STATES PATENTS

934,056	Ellis	Sept. 14, 1909
1,404,142	Riedel	Jan. 17, 1922
1,630,881	Zalocostas	May 31, 1927
1,828,270	Anderson	Oct. 20, 1931
2,069,174	Nielsen	Jan. 26, 1937
2,287,759	Hardesty et al.	June 23, 1942