

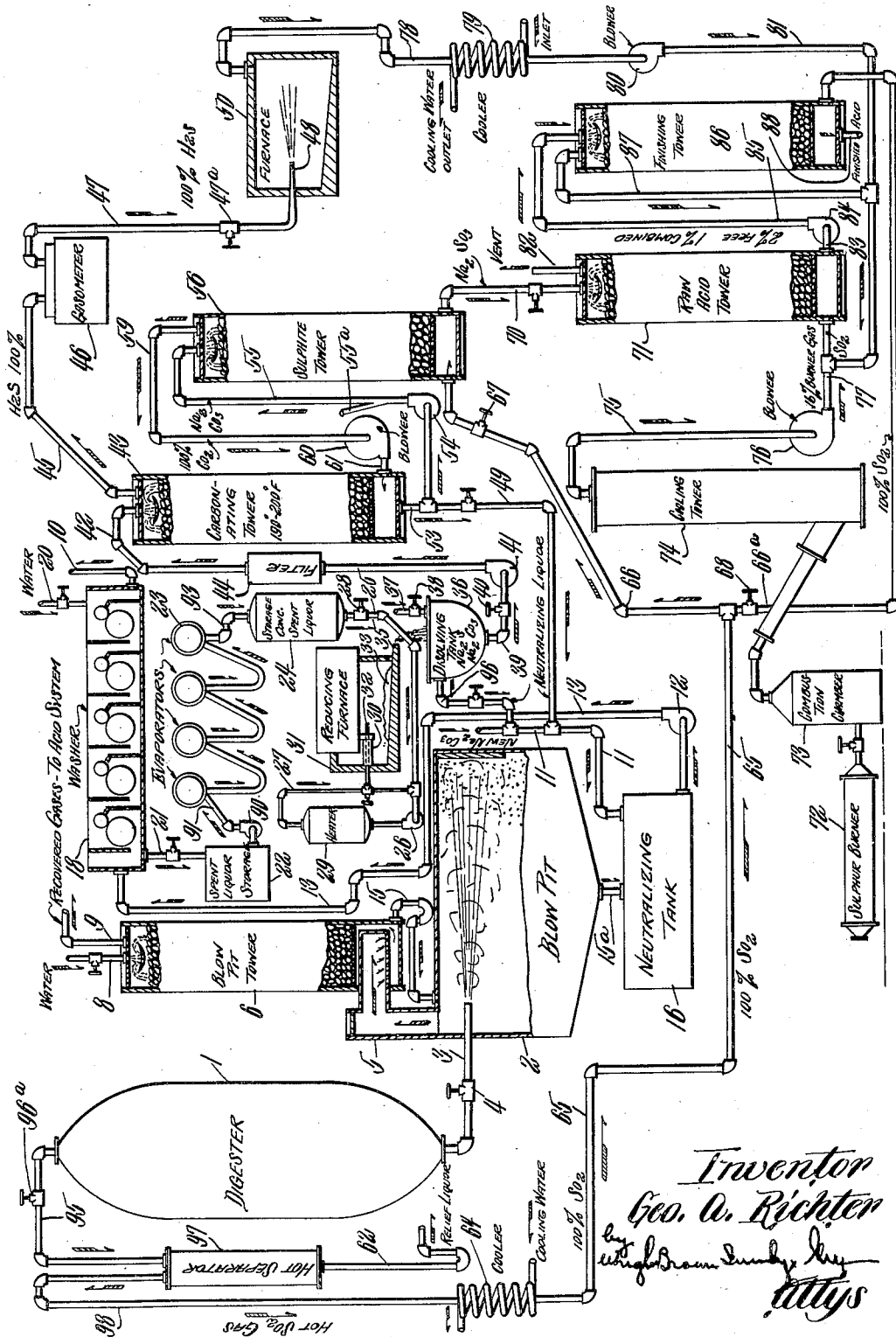
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CYCLIC PROCESS FOR THE PRODUCTION OF SULPHITE PULP

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CYCLIC PROCESS FOR THE PRODUCTION OF SULPHITE PULP

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This invention has relation to the production of sulphite pulp and has for its salient object to provide an efficient and cyclic process for such pulp production. In attaining this object, this invention provides for the utilization of the combustible content of the waste liquor for the generation of steam and power, for the recovery of the mineral or inorganic content of the waste liquor in the form of chemicals which may be utilized in the formation of fresh sulphite cooking liquor, and for the production of such fresh cooking liquor in a highly efficient manner. The process, thus, also eliminates the necessity for the pollution of rivers and streams by the discharge of waste or spent liquor thereinto, a nuisance thereby being avoided which is practically always present in the manufacture of sulphite pulp so-called. Other advantages attained in this invention will appear as the description proceeds.

For the cooking of the wood in the liberation of the cellulose fiber according to the present invention, I employ an acid sulphite liquor, comprising a soluble sulphite, preferably sodium sulphite, and free SO_2 in the form of sulphurous acid. Other soluble sulphites such as potassium, lithium, zinc and magnesium, while ordinarily commercially more expensive than sodium sulphite, may also be employed. Moreover the acid cooking liquor may contain varying proportions of combined and free SO_2 according to the character of the pulp which it is desired to produce or to economic expediency in the production of the liquor. For example, in the preparation of a pulp characterized by its high strength and pentosan content, as set forth in my application for U. S. Letters Patent Serial No. 749,564, filed No. 12, 1924, a "4-4" acid liquor, that is, a liquor containing about 4% free 4% combined SO_2 , may be employed. Or, if desired, an acid liquor containing 8% combined and 4% free, or a liquor having the usual SO_2 content of $\text{Ca}(\text{HSO}_3)_2$ cooking liquor and containing 1% combined and about 5% free SO_2 may be prepared.

The wood to be treated is placed in a digester which may be of the same character as that ordinarily employed in the manufac-

ture of sulphite pulp. The acid sulphite liquor may be heated directly, as by injecting steam into the digester, or if an indirect or "slow" cook is desired, in which case the cooking liquor is not diluted by the steam condensate, the liquor may be heated indirectly as by steam coils disposed in the digester, or by circulating the liquor from the bottom of the digester through a heater, wherein it is heated by steam coils or other suitable heating surface, to the top of the digester. After the cooking operation has been completed, as ascertained by tests made in the usual way from time to time, the digester is blown into a blow pit and gases arising from the discharged mass are passed through a condenser wherein the steam is condensed by direct contact with water and the chilled gases comprising SO_2 passing from the condenser are utilized in the preparation of fresh cooking liquor.

The spent liquor which is separated from the pulp and which contains sodium sulphite together with combustible organic compounds and spent sodium in the form of organic sodium compounds is now treated in a manner to regenerate such compounds economically in a form for utilization in the preparation of fresh acid cooking liquor. In such treatment, the waste liquor is evaporated to a certain degree of concentration and is then delivered to a retort wherein its combustible content is burned or consumed and its inorganic mineral content smelted in a reducing atmosphere and recovered in suitable form for subsequent treatment for the production of fresh acid cooking liquor, that is, substantially in the form of sulphite and carbonate. The smelt is dissolved in water and carbonated, as by bubbling carbon dioxide through the aqueous solution, thereby liberating hydrogen sulphide, and producing a sodium carbonate liquor which is then acidified with sulphur dioxide, producing a fresh acid cooking liquor. The carbon dioxide liberated in the acidification of the carbonate liquor is recovered and employed in the carbonation of other smelt liquor; and the hydrogen sulphide liberated in such carbonation is recovered, burned to sulphur dioxide

and utilized in the preparation of the fresh acid cooking liquor. The loss of sodium constituent in the cooking operation and recovery cycle is made up by the addition of the necessary sodium constituent in the form of sodium compounds, e. g., sodium carbonate, in the treatment or neutralization of the spent liquor, for the production of the fresh acid cooking liquor; and the loss in sulphur dioxide is made up by the gases produced by the combustion of sulphur or sulphur-bearing materials. In fact, after the process is in operation, practically the only raw materials which are needed for making up losses are sulphur or sulphur-bearing material, and either sodium sulphate, sodium sulphite, sodium carbonate, caustic soda, or sodium salts of a weak acid.

The invention may best be understood from the following more detailed disclosure thereof when considered in conjunction with the accompanying drawing, in which I have illustrated diagrammatically and conventionally various instrumentalities employed in the process.

Referring to the drawing, at 1 I have indicated the usual digester in which the cooking of the wood chips (spruce for example) may be effected. In carrying out the fiber liberation, the digester first is filled with wood chips and the necessary quantity of fresh acid cooking liquor (e. g., sodium sulphite comprising, say, 1% combined and 5% free SO_2 , though the proportion of combined and free SO_2 may be varied according to requirements) is then pumped into the digester. The digester cover is then tightly bolted or clamped on to the digester and, if a direct cook is being practiced, steam is slowly admitted into the digester until the temperature and pressure desired in cooking is reached, whereupon the cooking is continued for the requisite time period, tests being made in the usual manner until the cooking or fiber liberation has been completed. During the cooking operation, the digester is relieved as ordinarily, from time to time, and the relief gases are utilized for a purpose subsequently explained. After the cooking operation is completed, the contents of the digester are blown through a blow pipe 3, valved as at 4, into a blow pit indicated at 2. The blowing operation is accompanied by the formation and liberation of large quantities of steam or vapor and sulphur dioxide. These vapors and gases are conducted from the blow pit through the conduit or stack 5 into the lower portion of a direct condenser or "blow pit tower", indicated as a whole at 6. This condenser may be substantially like that illustrated in U. S. Letters Patent No. 1,469,958, granted to me October 9, 1923, and may contain a mass of inert interstitial material, such as spiral bricks, rocks, or the like, so that the vapors and gases are broken up

into multitudinous streamlets in passing upwardly through the interstitial material. Fresh cool water provided through a valved pipe 8 is sprayed into the top of the condenser and passing downwardly through the interstitial material therein, condenses the water vapor and cools the gas. Preferably the flow of water is so controlled that it leaves the condenser through a pipe 15, preferably discharging into the blow pit, at a temperature slightly less than its boiling point and thus containing only a slight amount of sulphur dioxide. The cooled gases containing about 30% to 60% SO_2 are conducted from the top of the condenser tower by a pipe 9 and may be utilized in the production of fresh cooking liquor, as will be explained.

As the spent sulphite liquor associated with the pulp in the blow pit is still acid, in order to avoid the necessity for acid-proof apparatus in subsequent operation, it is preferable to neutralize the acidity to a point of slight alkalinity by an alkali; and, for this purpose I preferably utilize an alkaline solution of caustic soda or sodium carbonate, or any other sodium salt of a weak acid, necessary to compensate for the losses encountered in the entire cycle, or if more alkali is necessary for the neutralization than required for make-up losses, it is furnished from a point in the cycle hereinafter described. In carrying out the neutralization, the sulphite stock together with its associated spent liquor is passed from the blow pit 2 through an outlet pipe 15a into a tank 16 which I may term for convenience the neutralizing and pulp storage tank, into which the neutralizing liquor is fed through a pipe line 11.

It is now necessary to separate the pulp from the spent liquor and to wash the pulp substantially free of liquor and entrained products of reaction prior to passage through the usual screens which are employed for refining the pulp and removing the so-called screenings therefrom, which consist of knots, shives, specks, particles of brick, cement, etc. For this purpose the pulp and waste liquor are forced by a pump 12 through a pipe 13 to a washing machine consisting of a series of pulp washers indicated conventionally at 18. The washing machine is preferably of the countercurrent type substantially like that illustrated and described in U. S. Letters Patent No. 1,421,664, to Brown, Martinson, Moore & Parker, dated July 4, 1922, although if desired the ordinary rotary vacuum type of washer may be employed. In the washer of the patent referred to, the pulp is carried continuously through tanks in one direction and the washing liquor is carried successively through such tanks in the opposite direction. The wash water is passed through a pipe 20 to the pulp delivered to the last washer of the series from which the washed pulp is delivered. The washed pulp may then be de-

livered to the usual screen (not shown) by a conduit 10. The wash water containing substantially all the spent liquor from the pulp is discharged from the first pulp washer of the series by a valved conduit 21 into a spent liquor storage tank 22 prior to the concentration thereof, from which it is drawn at the desired rate for evaporation and concentration. For the purpose I have illustrated conventionally at 23 a series of multiple effect evaporators, the details of construction of which it is unnecessary to describe. While I preferably employ multiple effect evaporators, any other form of evaporators for removing a part of the aqueous content of the liquor may be utilized. The liquor is drawn from the tank 22 by the pump 90 and delivered through a pipe 91 into the first effect of the multiple effect evaporator. From the last effect the liquor, which has been concentrated, say, to about 16° Baumé, and which contains about 25% solids, is passed through a pipe 93 into a storage tank 24, from which it is withdrawn for the combustion of the combustible content and the recovery of the inorganic compounds in the form of sulphide and carbonate.

The concentrated liquor in the tank 24 is now subjected both to heat and pressure to generate an explosive force therein, substantially as described in U. S. Letters Patent No. 1,326,414 to Moore & Quinn dated December 30, 1919. To this end the concentrated liquor is drawn from the tank 24 through a conduit 25 provided with a valve, as at 28, by a pump 26, and it is circulated through a circulation system comprising the pipe 27 and a heater 29. The liquor in passing under pressure through the circulating system is heated to a temperature above the boiling point by the heater 29 and is delivered from the circulating system through a pipe or series of valved pipes 30, terminating in nozzles 32 extending into a combined boiler furnace and retort indicated as a whole at 31. In the present instance it is desired that the sodium compounds recovered from the furnace should contain sodium sulphide and sodium carbonate. If this recovery takes place in a reducing atmosphere, there is no difficulty in recovering the desired salts, although there may be a slight accidental amount of adventitious sodium sulphate and sodium sulphite. One may, however, operate the furnace as most convenient, as the small amount of sodium sulphate is a harmless constituent and the sodium sulphite is not at all undesirable.

The furnace as shown is provided with a floor 33 which preferably extends rearwardly and downwardly from the front of the furnace into which project the nozzles 32 for the emission of the spent liquor. The floor at the rear wall of the furnace is provided with spouts 35 from which the molten effluent

escapes from the furnace. As indicated, an explosive force is generated in the waste liquor which is then disrupted and its combustible content burned and its inorganic mineral content smelted in the reducing atmosphere of the furnace as it leaves the nozzles.

The molten effluent from the furnace, consisting essentially of sodium sulphide and sodium carbonate, is delivered from the spouts 35 to a dissolving tank 36 and is dissolved in the desired amount of water supplied to that tank at seasonable temperatures from a suitable source through a water conduit 37 provided with a valve indicated at 38. A certain portion of the alkaline smelt liquor may be employed to neutralize the spent liquor in the neutralizing tank 16 when the alkaline solution containing sodium "make-up" compounds is insufficient for the purpose. In such case the necessary amount of smelt liquor is accordingly withdrawn from the dissolving tank and delivered through a valved pipe 96 into the pipe 11, from which the neutralizing compound is discharged into the tank 16. While such procedure may be followed in certain cases, owing to the fact that the smelt liquor reacts with the free sulphur dioxide in the spent liquor to form sodium thiosulphate and perchance to precipitate sulphur, such procedure is only optional, and I will presently describe a preferred procedure. In the optional treatment, the spent liquor after evaporation is also reduced substantially to sodium sulphide and sodium carbonate in the smelting retort, but there is also likely to be present adventitious amounts of other compounds which are not of advantage in the cooking process. The molten effluent delivered from the furnace into the dissolving tank produces a hot alkaline solution which may contain a certain amount of solid adventitious material. Such matter is preferably removed from the liquor by filtration prior to the carbonation thereof.

The carbonation is accomplished either by bubbling carbon dioxide gas obtained from any suitable source through the liquor or causing such liquor and carbon dioxide to pass in countercurrent flow through a suitable tower or series of towers containing inert interstitial material. The liquor containing this dissolved effluent from the combined boiler and furnace retort comprises, as has already been stated, essentially sodium carbonate and sodium sulphide, and the carbon dioxide by reaction with the sodium sulphide in solution converts the latter into sodium carbonate with the evolution of hydrogen sulphide gas.

In the present instance, the alkaline liquor is accordingly withdrawn for carbonation at the desired rate from the dissolving tank through a pipe 39, valved as at 40, by a circulating pump 41, and pumped successively through a filter 44, and thence through a pipe

42 to the top of a carbonating tower indicated as a whole at 43 which is supplied with carbon dioxide at its lower portion. The tower is filled with inert interstitial material, such as spiral brick, rock, and the like, and thus offers a large surface of contact between the alkaline liquor (which might have a tendency of plugging up the interstices of the interstitial material if it were not filtered), and the carbon dioxide. The carbon dioxide employed in the carbonation may be waste gas, diluted with other gases, such as the ordinary furnace flue gas or the waste carbon dioxide gas obtained from lime kilns in the decomposition of limestone in the manufacture of lime; but, as waste gas is usually contaminated with soot or other like dirty ingredients which tend to contaminate the liquor and because of the low concentration of carbon dioxide therein, is not to be preferred in the practice of the process. Moreover, even if the gas were scrubbed and cleaned, because of the presence of a high percentage of other inert gases, the hydrogen sulphide liberated in the carbonating process would be diluted by the inert gases introduced in the carbonating system with the carbon dioxide, so that it is difficult to burn, and even when it is subsequently burned in air and recovered in the form of sulphur dioxide, the sulphur dioxide is so dilute as to be of comparatively low value in the preparation of fresh acid cooking liquor. Hence, according to the present invention I provide for the carbonation of the alkaline smelt liquor with clean and substantially 100% carbon dioxide gas obtained in the acidification of the sodium carbonate, as will presently be explained. By employing such a strong, clean carbon dioxide, a smaller carbonating apparatus is required due to the increased rate of carbonation, subsequent filtration of the liquor or purification and cooling of dilute waste are avoided, and a strong, substantially 100% H_2S gas is produced which may be burned in atmospheric air to produce a sulphur dioxide gas which is almost as strong as sulphur burner gas and which may be employed together with the burner gas in the acid system. The strong carbon dioxide is passed, as already indicated, into the lower portion of the tower 43, is broken up into multitudinous streamlets by the inert interstitial material, and comes into intimate contact with and in countercurrent flow to the downwardly flowing alkaline liquor distributed at the top of the tower. The rate of feed of the alkaline liquor and the amount of carbon dioxide employed are controlled by suitable valves and speed controlling devices for the pumps, so that a liquor which is substantially 100% carbonated is produced without the introduction of excess carbon dioxide, and so that the hydrogen sulphide which is liberated in all parts of the tower and passes upwardly to the

top thereof is not diluted by excess carbon dioxide. The substantially 100% hydrogen sulphide is conducted from the top of the tower through an outlet pipe 45 into a gas container or gasometer indicated conventionally at 46, from which it is drawn to be burned and recovered as sulphur dioxide. The hydrogen sulphide is supplied from the gasometer at the desired pressure and velocity through a gas pipe or pipes 47, provided with regulating valves as at 47a, and terminating in nozzles, burners, or jets 48, extending into a gas furnace indicated as a whole at 50. The hydrogen sulphide gas issuing from the nozzles is burned in the presence of air to form sulphur dioxide and water, the amount of air introduced into the furnace being accurately regulated for such combustion without the introduction of unnecessary diluting air. The resultant gas after cooling contains about 10% to 11% SO_2 and may be commingled with the cooled and more or less purified sulphur burner gases, and utilized in the acid system, as will presently appear.

The sodium carbonate solution falling to the bottom of the tower is now in a condition to be acidified with sulphur dioxide. As previously indicated, if the make-up alkaline solution in the neutralizing tank is insufficient for the neutralization of the spent digesting liquor, alkali is provided from the cycle per se. The carbonate liquor is employed in assisting the neutralization, in preference to the smelt liquor, and I have accordingly indicated a valved conduit 49 through which the portion of the liquor necessary for neutralization is bypassed from the main outlet pipe line 53, to the pipe 11, discharging neutralizing liquor into the neutralizing tank 16. The main portion of the sodium carbonate liquor, however, is withdrawn from the carbonating tower through the outlet pipe 53 by a pump 54 and conducted through the pipe 55 to the top of an acidifying or "sulphite" tower indicated as a whole at 56. While, for simplicity, I have shown a single acidifying tower, it is to be understood that any suitable methods or means for the acidification of the sodium carbonate may be employed. For example, the acidification may be effected as by bubbling sulphur dioxide through the aqueous solution of sodium carbonate or by passing the solution through two or more towers arranged in series. Before passage into the sulphiting tower, however, it may be desirable to bleed in a small quantity of chlorine into the pipe 55 through a pipe 55a to oxidize any adventitious small amount of sodium sulphide contained in the carbonate liquor due to incomplete carbonation in the carbonating tower, to sodium sulphite or sulphate. This prevents the reaction of the sodium sulphide with sulphur dioxide in the acidifying or sulphite tower to form sodium thiosul-

phate or the precipitation of sulphur, which might give rise to objectionable mercaptan odors or discolor the pulp in the digesting process. The sulphite tower is filled with inert interstitial material such as spiral brick, field rock, or the like, and the carbonate liquor sprayed thereonto passes downwardly through the tortuous passages in the interstitial mass, and comes into intimate contact with sulphur dioxide passed into the bottom of the tower in countercurrent flow thereto.

The sulphur dioxide employed in the acidification of the carbonate may be derived from any suitable source, as for example sulphur burner gas or blow pit gas, but in the present case I preferably employ substantially 100% sulphur dioxide gas obtained from the relieving operation of the sulphite digesters. In this connection, it may be stated that while I have conventionally indicated one digester, I desire to have it understood that the process is ordinarily practised where there is a battery of digesters in operation so that relief gas may be available practically at all times. The sulphur dioxide displaces the less strongly acidic CO_2 radical in solution liberating carbon dioxide gas in all parts of the tower. The substantially 100% SO_2 gas is preferably so regulated and controlled that all the carbon dioxide is displaced from the carbonate solution producing a normal sulphite salt in solution containing an immaterial amount of free SO_2 , since a free SO_2 content in such liquor may be subsequently produced by weaker sulphur dioxide gas, as will be described. Since practically no dilute gas is introduced into the sulphite tower, the carbon dioxide liberated therein is also undiluted, and passes upwardly to the top thereof and is employed in the carbonating tower 43. For this purpose the carbon dioxide is conducted from the top of the tower by the pipe 59 and is blown as by a fan blower 60 through a conduit 61 into a lower portion of the tower 43. In other words, the carbon dioxide serves as a carrier for the SO_2 to the sodium sulphide of the smelt solution and is again liberated as CO_2 to again pass through the same cycle. By employing a substantially 100% sulphur dioxide in acidification, the reaction with the carbonate solution takes place more rapidly, and a smaller acidifying apparatus is necessary than if a dilute sulphur dioxide gas were employed in such acidification.

The relief gas from the digester employed in the acidification of the carbonate liquor is obtained, as indicated, during the relieving operation of the sulphite digester. The relief gas, however, emerges hot and moist from the digester so that provision must be made to separate the sulphur dioxide from the steam and entrained cooking liquor prior to use in the acid system. On the drawing, I have conventionally indicated a relief pipe 95, provided with a relief valve 96a through

which the relief gases pass into a trap or separator 97 wherein the entrained digesting liquor is separated from the hot gas. The "relief liquor" passes from the separator through the outlet pipe 62 and is discharged into the neutralizing tank 16 or the blow pit 2 for the recovery of valuable constituents. The hot and moist relief gas passes from the separator through an exit pipe line 98 into an indirect or surface cooler indicated, as a whole, conventionally, as a double pipe worm or coil cooler 64, wherein the vapors are condensed and the sulphur dioxide cooled. Any other suitable cooling surface and method for cooling the relief gas may be employed, as, for example, the method and apparatus described in my application for U. S. Letters Patent Serial No. 26,363, filed April 28, 1925. The cooled relief gas consisting of substantially 100% SO_2 passes from the cooler 64 through the conduit 65 and divides into two branches, namely, the branch 66, valved as at 67, for supplying the acidifying tower with a predetermined and regulated amount of strong sulphur dioxide as has been previously indicated, and the branch 66a, valved at 68, for supplying the finished acid-making system with strong sulphur dioxide as will presently be indicated.

The strong normal sodium sulphite solution falling to the bottom of the acidifying tower is delivered to another acidifying system wherein the sulphite liquor is again treated with sulphur dioxide to build up the desired free SO_2 content therein. Any suitable system or method for acidification may be employed as by bubbling SO_2 through the normal sulphite solution or by passing the solution successively through two or more towers arranged in series. As shown, the normal sulphite liquor is withdrawn from the acidifying tower through the valved pipe 70 and passed into the top of an acidifying or "raw acid tower" 71, supplied with sulphur dioxide at its lower portion. The tower 71 is filled with inert interstitial or surface material and the liquor passes downwardly through tortuous or winding passages intimately contacting with the sulphur dioxide passed upwardly in countercurrent flow thereto.

The sulphur dioxide employed in the preparation of the raw acid liquor is preferably that obtained in the combustion of sulphur or sulphur-bearing material and in the combustion of the hydrogen sulphide from the carbonating tower, together with, if desired, the recovered blowpit sulphur dioxide gas. For this purpose, as indicated on the drawing, sulphur or sulphur-bearing material is burned as in a rotary sulphur burner 72, and the products of combustion pass therefrom through a combustion chamber 73, wherein the conversion of the sulphur vapor to sulphur dioxide is completed to produce a gas

comprising about 16% sulphur dioxide, and thence through a cooling and scrubbing system indicated conventionally as a whole at 74 wherein the gases are more or less cooled and purified. The cooled burner gases are drawn from the cooling system through a conduit 75 by a blower 76 and forced through a conduit 77 into the lower portion of the raw acid tower 71.

Similarly, the gases resulting from the combustion of the hydrogen sulphide in the gas furnace 50 pass therefrom through a conduit 78 and a suitable cooling surface, as for example a double-pipe type worm cooler indicated conventionally at 79. The water vapor contained in the burned hydrogen sulphide gas is condensed, resulting in a 10% to 11% SO_2 gas which is drawn from the cooler by a fan 80, and forced through the conduit 81 into the conduit 77 and into the tower 71 along with the sulphur burner gas. At ordinary temperature and atmospheric pressure, by regulating the flow of gases from the sulphur burner, the hydrogen sulphide furnace, and the gas obtainable from the blow pit, and also the rate of flow of the normal sulphite solution delivered at the top of the tower 71, with a normal sulphite liquor containing 4% combined SO_2 , a raw acid liquor containing 6% to 7% free SO_2 can be produced, and with a sulphite liquor containing 1% combined SO_2 , a raw acid liquor containing 2.5% free SO_2 can be produced. Any inert gases unabsorbed by the normal sulphite solution in the tower 71 are allowed to escape through an outlet or vent 82.

In certain cases it may be desirable to cook in an acid liquor having a very high free SO_2 content. In such cases, the raw acid liquor produced in the tower 71 is withdrawn therefrom and passed to a fortifying system wherein the liquor is suitably treated with concentrated sulphur dioxide. To this end the liquor is conducted from the lower portion of the tower by an outlet pipe 83 and forced by a pump 84 through a pipe 85 to the top of a fortifying or finishing tower, indicated as a whole at 86, supplied with substantially 100% SO_2 at its lower portion, as from the branch line 66a previously referred to. The tower is filled with inert interstitial or surface material such as spiral brick, field rock, or the like. The relief gas may be commingled, if desired, with a portion of the recovered blowpit gas from the pipe 9 not required by the raw acid liquor system. The downwardly flowing raw acid liquor comes into intimate and countercurrent contact with the upwardly flowing relief gas over the large surface of interstitial material for a sufficient period of time to produce an acid liquor containing a maximum SO_2 content at atmospheric pressure and ordinary temperature. Any unabsorbed gas at the top of the relief tower is bypassed through a conduit

87 and bled into the conduit 81 discharging into the raw acid tower. With a raw acid liquor containing about 1% combined SO_2 , by regulating the flow of relief gas into the tower and the amount of raw acid distributed at the top of the tower 86, a finished cooking acid liquor containing 5% free SO_2 may be produced, and similarly with a raw acid liquor containing 4% combined SO_2 , a finished acid cooking liquor containing 7% to 8% free SO_2 may be produced. The finished acid liquor falling to the bottom of the tower 86 is withdrawn through an outlet pipe 88 and may be delivered into storage tanks from which it may be pumped for use in the digesters.

Before concluding it may be stated that in a plant where a "4-4" acid, that is, an acid containing 4% combined and 4% free SO_2 , is employed or, in any other case, where the free SO_2 is equal to, or less than, but not in excess of the combined SO_2 , the necessity for an acid finishing tower is eliminated. Moreover, in such cases, the necessity for cooling the liquor or the sulphur dioxide gas from the various sources is also eliminated, and the sulphur dioxide gases from all the sources may be combined in hot state and passed into the raw acid liquor tower, the amount of sodium carbonate liquor introduced into the sulphite tower and the rate of flow of the sulphur dioxide gas passed thereinto being controlled and regulated to produce an acid sulphite liquor of the desired strength. Such procedure is possible, owing to the fact that sodium bisulphite is a stable compound and there is a tendency for its formation in solution even at an elevated temperature. Thus, in such cases, less apparatus is needed than where a higher free than combined SO_2 content is necessary in the finished acid cooking liquor. Moreover, where a "4-4" or other acid cooking liquor having a high combined SO_2 content is employed, a substantial amount of spent liquor and all the relief liquor may be reemployed in digestion of other raw cellulosic material, since these liquors contain substantial amounts of unspent combined and free SO_2 , thus allowing a conservation of heat and chemicals to be practiced in connection with the process. However, as stated, the maximum amount of free SO_2 is determined by the formula of the sodium acid sulphite: that is, the maximum free SO_2 content obtainable is equal to the combined SO_2 , plus the slight solubility of the SO_2 at that particular elevated temperature.

At the risk of repetition, it may be stated that while I have confined myself to a more or less detailed description of a preferred procedure and a preferred apparatus therefor, this was by way of illustration only; and that this invention is capable of various changes and modifications which are within

its spirit and scope as defined by the appended claims. It may be also again stated that the drawing is diagrammatic and conventional, no attempt being made to show the relative sizes or true location of the various instrumentalities. For the sake of clarity in the drawing, certain details of construction have been omitted, but it will of course be understood that valves for the pipe lines, pumps, and fans for maintaining flow or circulation through the system, storage tanks, or any other construction will be supplied where necessary.

What I claim is:

1. A cyclic process which comprises cooking raw cellulosic material in a sulphurous acid solution of alkali sulphite, smelting the inorganic content of the spent cooking liquor in a reducing atmosphere to produce alkali sulphide and alkali carbonate, dissolving the smelted compounds in water, carbonating the solution to convert the alkali sulphide into alkali carbonate, treating the carbonated solution with a water-soluble oxidizing agent to oxidize such residual alkali sulphide as may be present therein to an oxygen-containing salt of the nature of alkali sulphite and alkali sulphate, and acidulating the resulting solution with sulphur dioxide to form a fresh liquor for repeating the cooking step of the cycle.

2. A cyclic process which comprises cooking raw cellulosic material in a sulphurous acid solution of alkali sulphite, smelting the inorganic content of the spent cooking liquor in a reducing atmosphere to produce alkali sulphide and alkali carbonate, dissolving the smelted compounds in water, carbonating the solution to convert the alkali sulphide into alkali carbonate, treating the carbonated solution with chlorine water to oxidize such residual alkali sulphide as may be present therein to an oxygen-containing salt of the nature of alkali sulphite and alkali sulphate, and acidulating the resulting solution with sulphur dioxide to form a fresh liquor for repeating the cooking step of the cycle.

3. In a cyclic process which involves cooking raw cellulosic material in a sulphurous acid solution of alkali sulphite and releasing sulphur dioxide from the solution during the cooking operation, those steps which comprise smelting the inorganic content of the spent cooking liquor to produce alkali sulphide and alkali carbonate, dissolving the smelted compounds in water, carbonating the smelt solution with strong carbon dioxide to convert its alkali sulphide content into alkali carbonate and to liberate strong hydrogen sulphide, treating the carbonated solution with the sulphur dioxide released during the cooking operation to form alkali sulphite solution and to liberate strong carbon dioxide, using said liberated carbon dioxide for the aforesaid carbonating treat-

ment, burning said strong hydrogen sulphide into sulphur dioxide, and treating the alkali sulphite solution with said last-mentioned sulphur dioxide to form a fresh cooking solution.

In testimony whereof I have affixed my signature.

GEORGE A. RICHTER.