

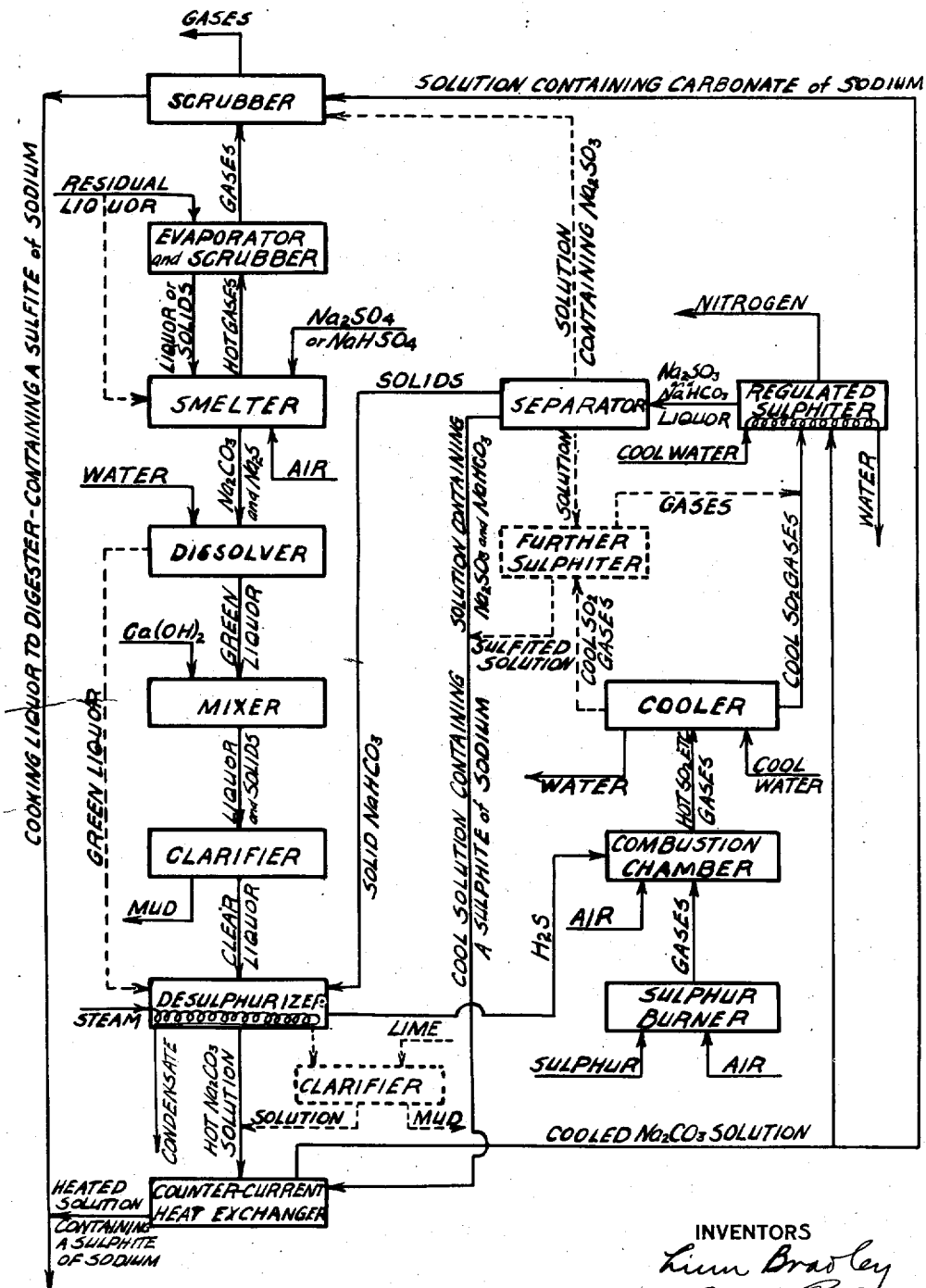
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## PRODUCTION OF PULP AND TREATMENT OF RESIDUAL LIQUORS, ETC

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## UNITED STATES PATENT OFFICE

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PRODUCTION OF PULP AND TREATMENT OF  
RESIDUAL LIQUORS, ETC.

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This invention relates to the treatment of alkali-metal compounds, particularly alkali-metal carbonates and sulfur-bearing compounds of alkali-metal.

This invention relates, more particularly, to improvements in the production of pulp and in the production of chemicals, for example from the residual liquors of a pulp making process for use in producing liquors for use in carrying out a pulp making process. The invention includes improvements in the cooking of wood, etc. for the production of chemical pulp; in regenerative or cyclic methods of pulp production with regeneration of cooking liquors from residual liquors of the same or different related processes; in new combinations of pulp making processes; in the production of alkali-metal compounds; in the treatment of residual liquors for the production therefrom of alkali-metal compounds or of cooking liquors, etc.

The present invention includes a process for converting a sulfide of an alkali-metal into a carbonate of an alkali-metal, e. g. sodium carbonate, in which the sulfide is treated with a suitable acidic material such as available carbon dioxide in a non-gaseous form, and in which a volatile sulfide, e. g. hydrogen sulfide, is produced and removed.

The present invention also includes a process for the production of a sodium acid carbonate in a solid state, and a process in which solid sodium acid carbonate is utilized in the treatment of solutions containing sodium sulfide to form a carbonate of sodium and hydrogen sulfide.

The invention also includes a process of treating admixed sodium carbonate and sodium sulfide, such, for example, as results from a strongly reducing furnace treatment of material derived from residual liquors from a pulp making process in which sodium-sulfur compounds are employed, for the production of liquors containing a sulfite of sodium, in which process the treatment of a solution of such sodium carbonate and sodium sulfide is so conducted as to convert the sodium content of the sodium carbonate and the sodium sulfide largely into a sulfite of sodium, and in which the formation of sodium thiosulfate is regulated or may even be substantially prevented.

The invention also includes cyclic or regenerative processes for producing pulp from wood, etc., as well as interrelated processes for producing pulp, in which, or in some of which processes, a digesting liquor is employed which includes a sulfite of sodium, and in which the residual liquor is treated to regenerate or reform a digesting

liquor for use in the same or a related process, particularly a digesting liquor which contains a sulfite of sodium, and which may or may not contain sodium thiosulfate in regulated lesser amount, e. g. less than the amount of the sulfite of sodium, and in which the resulting digesting liquor is employed for digesting wood, etc. for the production of pulp therefrom.

The invention includes improvements in the production of liquors containing a considerable amount of a sulfite of sodium, with little if any, or with only regulated lesser amounts of, sodium thiosulfate, by utilizing the sodium content of liquors which contain considerable amounts of sodium carbonate and of sodium sulfide.

The invention includes various improvements in the above and other processes, which will more fully appear from the following more detailed description.

The present application is a continuation in part of our prior applications now matured to patent: Serial No. 704,176 filed April 4, 1924 (Patent 1,896,038); Serial No. 713,257 filed May 14, 1924 (Patent 1,898,613); Serial No. 133,289 filed Sept. 2, 1926 (Patent 1,795,754); Serial No. 133,290 filed Sept. 2, 1926 (Patent 1,870,944); and Serial No. 686,137 filed Jan. 14, 1924 (Patent 1,833,313).

When wood, etc. is cooked or digested with a cooking liquor containing sodium-oxy-sulfur compounds, such as a sulfite of sodium, and when the residual liquor from such cooking process is suitably concentrated and the resulting solid material heated in a calcining or/and smelting furnace to decompose sodium-organic compounds, etc., the sodium compounds are converted largely into sodium carbonate and sodium sulfid, particularly if the furnace operation is carried out under suitable reducing conditions toward and near the end of such furnacing treatment, e. g. by heating the sodium compounds to a temperature sufficient to melt them and in the presence of incandescent carbon in sufficient amount to insure the sodium-sulfur compounds in the furnace product being largely, if not entirely, in the form of sodium sulfid. A concentrated aqueous solution of the sodium compounds present in such a furnace product will usually contain a large amount of sodium carbonate and of sodium sulfide and usually with the former being in larger amount than the latter.

The present invention includes improvements in such processes in which such a solution containing sodium carbonate and sodium sulfide is produced. According to the present invention, 55

such solutions may be treated for the conversion of some of the sodium content of the sodium carbonate and sodium sulfide into a sulfite of sodium, without the formation of large or prohibitive

5 amounts of sodium thiosulfate during the treatment. Such treatment may be a direct or an indirect treatment which may be considered an oxidizing treatment in the sense that sodium sulfide is converted at least in part into a sulfite of sodium. The present invention includes improvements in both indirect and direct treatment of such sodium sulfid, as well as combined indirect and direct treatment of the nature of oxidation treatment for producing solutions containing a sulfite of sodium either without or with regulated lesser amounts of sodium thiosulfate, sodium carbonate and sodium sulfide.

10 The present invention includes improvements in the treatment of solutions including sodium carbonate and sodium sulfide with carbon dioxide, and particularly with available carbon dioxide supplied to the sulfide of sodium in a non-gaseous form and advantageously and preferably in sufficient amount to convert most of the sodium sulfide into a carbonate of sodium and to convert sulfur thereof into a volatile sulfide, with removal of volatile sulfide from a carbonate of sodium remaining with the liquor.

15 While, in its broader aspects, the invention includes improvements in the carbonating of solutions containing a soluble alkali metal sulfide with carbon dioxide supplied to the solution in gaseous form, particularly in combination with other features of the process, the invention includes improvements broadly in the carbonating of such solutions with available carbon dioxide supplied to the alkali-metal sulfide in a non-gaseous form.

20 Thus the available carbon dioxide may be supplied in the form of a suitable carbonate or bicarbonate or other form such that available carbon dioxide thereof will react with sodium sulfide during the process. A particularly advantageous means of supplying available carbon dioxide is a sodium acid carbonate, or other acid carbonates which give up some of their carbon dioxide content so as to react with the sodium sulfide to form a carbonate of sodium and to release sulfur of the sodium sulfide in the form of a volatile sulfide. A bicarbonate such as sodium bicarbonate is a particularly advantageous material to employ, and the invention includes an improved method of treating solutions including sodium sulfide, with sodium bicarbonate to form sodium carbonate and to set free hydrogen sulfide. In referring to available carbon dioxide, we refer to the carbon dioxide content of such carbonate, etc. which is available to react with sodium sulfide to release sulfur therefrom and form a carbonate of sodium. Thus in sodium bicarbonate,  $\text{NaHCO}_3$ , one half of its carbon dioxide content is considered to be available carbon dioxide. Other suitable acid carbonates of alkali metals can be employed.

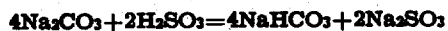
25 In treating liquor including sodium carbonate and sodium sulfide with available carbon dioxide supplied in the form of a sodium acid carbonate, the liquor may be mixed with the required amount of the sodium acid carbonate, e. g.  $\text{NaHCO}_3$ , which may advantageously be employed in the form of solid sodium bicarbonate, and the resulting admixture can then be agitated and subjected to reduced pressure or/and heated so as to remove hydrogen sulfide which results from the interaction between the available carbon dioxide

of the sodium acid carbonate and the sodium sulfide. The following assumed equations will serve to illustrate the reactions that may take place.



5 In using solid sodium acid carbonate it may advantageously be added in somewhat larger amounts than called for by these equations, e. g. 10 up to twice as much, more or less, especially when it is desired to effect a substantially complete elimination of the sulfide sulfur from the solution as a volatile sulfide.

15 The present invention also includes an improvement in the production of sodium acid carbonate, e. g. sodium bicarbonate, which may be used in the treatment of such sodium sulfide containing liquors, as well as an improvement in a combined process during part of which the sodium acid carbonate is produced, and during part of which the sodium acid carbonate so produced is employed for thus treating the sodium sulfide-containing liquors. In its broader aspects, and particularly in connection with the part of the process in which the solid sodium acid carbonate is employed for treating the sodium carbonate-sodium sulfide liquors, the solid sodium acid carbonate may be obtained in any suitable manner, and by a method other than those included as part of the invention. The solid sodium acid carbonate can, however, be advantageously obtained by a regulated sulfiting treatment of a suitably concentrated solution including sodium carbonate, preferably free or substantially free from sodium sulfide and from sodium thiosulfate. By effecting a regulated sulfiting of such a solution a solid sodium acid carbonate can be produced and the latter can be separated from the solution in solid form. The regulated sulfiting treatment is preferably conducted at a temperature below that at which sodium bicarbonate readily breaks up and releases carbon dioxide. The sodium carbonate material being sulfited is advantageously maintained at a temperature considerably below  $60^\circ \text{C}$ . in order to deposit as much solid sodium acid carbonate as may be needed or is practicable. A solid carbonate of sodium may advantageously be present in the concentrated solution which is to be sulfited, so that the admixed solution and the solid carbonate of sodium form a slurry. When using such a slurry containing a solid carbonate of sodium, a relatively large amount of solid sodium acid carbonate can be prepared by regulating the sulfiting step so as to convert the desired amount of soda into sodium sulfite while keeping the materials cool enough to avoid objectionable decomposition of the sodium acid carbonate formed, and cool enough to deposit as much of the sodium acid carbonate as a solid as can be readily and practically done. Thus temperatures considerably below  $60^\circ \text{C}$ . are advantageously employed, e. g. between  $5^\circ$  and  $50^\circ \text{C}$ . The regulated sulfiting step may be indicated by the following assumed equation, although not limited thereto.



25 The resulting sulfited liquor contains sodium sulfite in solution. This solution may be separated from the solid sodium acid carbonate in any suitable and convenient manner and the sodium acid carbonate (preferably after suitably washing to remove sodium sulfite) is then available for use for the treatment of the sodium sul-

fide containing solution to convert sodium sulfide into a carbonate of sodium and to set free sulfur of the sodium sulfide in the form of hydrogen sulfide.

5 In its broader aspects, the solution or liquor which is to be treated with the sodium acid carbonate (or with available carbon dioxide supplied in other suitable form), and which usually contains more sodium carbonate than sodium  
10 sulfide, can be obtained from any suitable source and in any suitable manner. However, such liquor is advantageously obtained by dissolving sodium compounds contained in a furnace product derived from residual liquor produced in the  
15 cooking or digesting of wood, etc., with cooking liquor which contains a sodium-oxy-sulfur compound, such as a sulfite of sodium. Ordinarily and advantageously the liquor to be treated will have a greater amount of sodium present as sodium carbonate than as sodium sulfide. However,  
20 it is an advantage to have a rather large amount of sodium sulfide present when the sulfur is to be removed as hydrogen sulfide and such hydrogen sulfide is to be burned to form sulfur dioxide and the latter is to be employed for a sulfiting  
25 treatment, e. g. to convert a carbonate of sodium into a sulfite of sodium, especially when the sulfite of sodium is to be used as the principal reagent in the digestion or cooking of wood, etc., as herein described.

30 When wood is cooked or digested to produce chemical pulp with a cooking liquor including a considerable amount of sodium sulfite, either alone or with moderate amounts of other chemicals, such as sodium hydroxide, sodium sulfide,  
35 sodium sulfate, sodium thiosulfate, sodium carbonate, sodium bisulfite,  $\text{H}_2\text{SO}_3$ , etc., and the residual liquor from the cooking or digesting operation is concentrated and the resulting dried  
40 product is calcined and/or smelted in the presence of incandescent carbon to convert the sodium compounds largely into the form of sodium carbonate, a considerable proportion of the soda  
45 in the furnace product is present as sodium sulfide, particularly when the latter period of the furnacing operation is carried out under strongly reducing conditions. When the soda-containing  
50 furnace product or melt is leached by or dissolved in a small amount of water, the resulting solution will contain a large amount of sodium carbonate and sodium sulfide. Such solutions, so obtained, which include sodium compounds derived from such residual liquor may  
55 be advantageously treated according to the present invention for the reproduction or regeneration of cooking liquor for use in the same process or a related process.

The sodium carbonate-sodium sulfide liquor may require clarifying, before it is further treated, for instance when it contains carbon resulting from a strongly reducing furnace treatment  
60 in which oxy-sulfur compound or compounds of sodium are reduced by incandescent carbonaceous matter to form sodium sulfide. Such liquor may be clarified by filtering or otherwise, either before  
65 or after its treatment with the available carbon dioxide and the removal of volatile sulfide formed. The liquor may thus be treated with the available carbon dioxide to form a carbonate of sodium and a volatile sulfide, after which it is more  
70 suitably filterable through cotton fabric while hot and is less destructive upon such fabric because of the preliminary decomposition of the sodium sulfide in the liquor.

75 The liquor, after the carbonating and related

treatment under conditions to remove substantially all or at least a major portion of the sulfide-sulfur as a volatile sulfide, may be cooled, if needed, by any suitable means down to a temperature which is suitable and advantageous for the regulated sulfiting step in which solid sodium  
5 acid carbonate is formed and separated from the liquor. A heat interchanger may, if desired, be employed so as to preheat sodium sulfite liquor with such a warm sodium carbonate containing  
10 liquor. The sodium sulfite liquor remaining after the separation of solid sodium acid carbonate formed in the sulfiting step may thus be caused to pass countercurrent to a warm sodium carbonate liquor resulting from the carbonating  
15 and volatile sulfide-removing step or steps of the process. A portion or all of such sodium sulfite liquor may be thus employed for cooling such a sodium carbonate liquor.

In the combined process of the present invention, the sodium carbonate-bearing liquor from  
20 which part or all of the sulfide-sulfur has been eliminated, is advantageously subjected to a regulated sulfiting treatment to produce solid sodium acid carbonate and to produce a liquor containing sodium sulfite together with a small but regulated amount of a carbonate of sodium, which  
25 liquor can be advantageously employed as it is or modified to produce a cooking liquor for use in the cooking of wood, etc. in carrying out the cyclic or inter-related pulp making process;  
30 and residual liquor from such a process can advantageously be treated in such a way as to produce a furnace product or melt from which a solution of sodium carbonate and sodium sulfide  
35 may be obtained, and which may then be treated by the carbonating and related steps of the process to remove sulfide-sulfur and to produce a carbonate of sodium solution free or relatively  
40 free from sulfide-sulfur, which solution may then be subjected to a regulated sulfiting treatment for the production of solid sodium acid carbonate and a solution containing sodium sulfite and  
45 some carbonate of sodium, which may be used in a further step or steps in carrying out the cycle or inter-related process or processes.

The regenerated cooking or digesting liquor may be alkaline, neutral or acid to litmus when  
50 charged into the digester for the cooking operation. Such digesting liquors may contain substantially only normal sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) as the digesting agent, or they may comprise variable mixtures of normal sodium sulfite and sodium acid sulfite, or they may in some cases  
55 contain only or mainly sodium acid sulfite ( $\text{NaHSO}_3$ ) as the digesting agent, or they may contain both sodium acid sulfite and excess sulfurous acid. Instead of containing some sodium acid sulfite, the digesting liquors may be either  
60 alkaline or neutral to litmus and may contain a suitable compound or compounds, in suitable proportions and amounts, such as sodium sulfite, sodium hydroxide, sodium thiosulfate, sodium sulfide, sodium sulfate, sodium carbonate, etc.

Where the cooking liquor contains sodium  
65 monosulfite in sufficient amount it may also contain a lesser and regulated amount of sodium thiosulfate, as explained in our prior applications, Serial No. 704,176 and 713,257; and the present invention enables the amount of sodium thiosulfate present in such cooking liquors to be regulated and controlled.

The present invention is particularly advantageous in cases where sodium thiosulfate is not  
75 desired or permissible in the cooking liquor, or

where only a small and limited amount of thiosulfate is to be present therein. The process of the present invention enables a major part of the sulfide sulfur to be removed from the carbonated liquors, and enables the resulting liquors to be sulfited so as to facilitate producing therefrom cooking liquors containing a moderate amount of, or substantially free from sodium thiosulfate.

The process of the present invention is particularly advantageous for use in a cyclic or regenerative process in which strongly acid sodium sulfite digesting liquors are employed. When the digesting liquors have a sufficient quantity of sodium sulfite, and the sodium sulfite is used in sufficient amount in proportion to the amount of the wood or other raw fibrous material digested, and when only a suitably regulated lesser amount of sodium thiosulfate is present, a superior result is obtained as compared to that obtained when the digesting liquor contains an excessive amount of sodium thiosulfate. This is true not only when the liquor is either neutral or alkaline to litmus, but it is particularly true when the digesting liquors are strongly acid to litmus at the time they are charged into the digesters in which the digesting or cooking operation takes place. In general, the larger the proportion of free or uncombined sulfur dioxide as compared with the combined sulfur dioxide (as sodium monosulfite), the greater the desirability of having the sodium sulfite in sufficient excess over the thiosulfate, so as to overcome the tendency of the latter to injure the quality of the fibrous material.

The present cyclic or regenerative process, in which sodium carbonate and sodium sulfite-containing liquors are carbonated and the carbonate of sodium thereafter sulfited, enables regenerated cooking liquors to be produced and employed substantially free from sodium thiosulfate, or containing only suitably limited and regulated amounts of sodium thiosulfate, and enables cooking liquors to be regenerated which are either neutral or alkaline to litmus, or which contain sodium bisulfite as well as sodium monosulfite and which may be acid to litmus, as well as cooking liquors containing mostly sodium bisulfite or containing sodium bisulfite with an excess of sulfurous acid beyond the bisulfite stage.

The reactions which take place during the digestion of wood, etc., with such sulfite of sodium cooking liquors (whether neutral, alkaline or acid to litmus) are such that a major portion of the sodium content of the residual liquor from the digesting treatment can be readily converted by evaporation, calcination and smelting, into a product consisting mainly of sodium carbonate and sodium sulfide; and a solution of such sodium carbonate and sodium sulfide can then be treated by the carbonating, volatilizing and sulfiting treatments of the present invention for the regeneration of further amounts of suitable cooking liquors which include a sulfite of sodium.

The cyclic or regenerative process is particularly applicable to the cooking of wood to produce pulp therefrom, but in some of its broader aspects it is also applicable to the digesting or cooking of other cellulosic-fibre bearing materials which can be digested or cooked to render soluble a sufficient portion of the non-fibrous organic materials thereof so as to render fibres readily separable from each other by mechanical treatment.

After the wood or other material has been digested or cooked to the required extent by such a digesting liquor, e. g., containing a sulfite of sodium, the resulting residual liquor may be sep-

arated from the fibrous material. If the residual liquor is acid to litmus, it may, if desired, be made either neutral or alkaline to litmus by adding a sufficient amount of a suitable alkaline material thereto, e. g., a carbonate of or/and a sulfite of sodium, which may advantageously be some of the sodium carbonate and sodium sulfide which is obtained by the step or steps of the complete process of the cycle in which residual liquor is concentrated and sodium compounds are furnished under reducing conditions. Such addition of alkaline material, in case such material is added to residual liquor, may be made either before or after effecting a partial concentration of the residual liquor, either without or advantageously with some admixed washings. Ordinarily, however, such addition is made before concentrating such residual liquor although when it is desired to recover some sulfur dioxide from such a residual liquor, the addition of alkaline material prior to such concentrating and recovery step may be advantageously dispensed with.

The residual liquor, after removal of water therefrom, is converted into a solid material which is subsequently subjected to a furnacing treatment advantageously under reducing conditions adapted to yield a furnace product containing sodium carbonate and sodium sulfide in rather large amounts. By having a relatively large amount of sodium sulfide in the furnace product, a considerable amount of a sulfite of sodium can be derived therefrom, by utilizing some of the sulfur content thereof in a regulated oxidation of such sulfide sulfur. Hence, it is desirable to so arrange and conduct the digesting and furnacing treatments that a considerable amount of sulfur is present in the furnace product as sodium sulfide. The furnace product should preferably contain little if any thiosulfate, or polysulfide, and should contain mostly sodium carbonate and sodium sulfide, especially when the indirect method of oxidizing the sulfide sulfur to sulfite is employed. To aid in providing a considerable amount of sodium sulfide in the furnace product, a considerable amount of a sulfate of sodium can be furnished to the solids resulting from the evaporation of the residual liquor, e. g. by adding it either before, or at the time, or after such solids are charged into the furnace.

When sulfate of sodium or acid sulfate of sodium is added to and mixed with the sodium bearing material at some suitable point or points prior to completing the furnacing thereof in the reducing furnace, the added sodium sulfate will supply added sodium and added sulfur to the process to make up for some of the losses or/and to provide a surplus of soda over that required for use in liquor employed in a subsequent digesting operation. Additional carbonaceous material may, if necessary, be admixed with the furnace charge in which such sodium sulfate is included. During the strongly reducing furnacing operation, such sodium sulfate is largely reduced to sodium sulfide. By supplying a relatively large amount of a sulfate of sodium in this manner, it is possible to produce a furnace product containing a large amount of sodium sulfide as well as of sodium carbonate, from which, by subsequent treatment according to the invention, sodium carbonate or a sodium acid carbonate and sodium sulfite or an acid sulfite can be produced. Considerable amounts of a carbonate of sodium (e. g. sodium bicarbonate) can thus be produced for sale in conjunction with the

production of liquors which contain a sulfite of sodium and which are either free from or contain relatively small amounts of sodium thiosulfate. The sulfur content of the sodium sulfate is also made available to a considerable extent as sodium sulfide which can be converted by subsequent treatment into a sulfite of sodium, e. g., by carbonating the sodium sulfide and driving off hydrogen sulfide, burning or oxidizing the hydrogen sulfide to form sulfur dioxide, and employing sulfur dioxide, so produced, in a sulfiting step of the process to form a sulfite of sodium.

The hydrogen sulfide driven off during or subsequent to the carbonating treatment of the sodium sulfide may be burned to sulfur dioxide in a suitable combustion chamber, for example, a combustion chamber attached to and operated in conjunction with a sulfur burner, and the resulting sulfur dioxide may be utilized in the sulfiting step of the process and it may be supplemented by such additional sulfur dioxide as may be required therefor. It may be supplied, for example, by the burning of sulfur or suitable sulfides. This burning of such hydrogen sulfide to form sulfur dioxide, and the utilization of the resulting sulfur dioxide in the formation of a sulfite of sodium is an indirect oxidation of the sulfur of the sodium sulfide which may be accomplished without the formation of prohibitive amounts of sodium thiosulfate. By combining this indirect oxidation with the carbonate of sodium producing and utilizing steps of the process, an inter-related cyclic or indirect process is provided of a particularly advantageous character. The sodium sulfide is decomposed by a sodium acid carbonate, and sodium carbonate and hydrogen sulfide are formed. The hydrogen sulfide is removed and thereafter oxidized to form sulfur dioxide, which is thereafter recombined with the sodium carbonate or other sodium compound in a direct or indirect manner to form a sulfite of sodium. In this way, the sulfur may be oxidized from sulfide-sulfur to sulfite-sulfur without formation of prohibitive amounts of thiosulfate.

The invention will be further described in connection with certain specific embodiments thereof. In the carbonating step of the process, in which the sodium sulfide contained in the liquor is treated with available carbon dioxide in non-gaseous form, different carbonating materials can be employed. The use of a sodium acid carbonate or sodium bicarbonate is particularly advantageous, a carbonate of ammonium can also be employed and has certain advantages. In some cases, carbon dioxide can be dissolved in water or in the liquor and employed in the form of a solution. These and other novel features of the process will be illustrated by the following more detailed description.

According to one embodiment of the invention, solid sodium bicarbonate is added, small portions at a time, to a concentrated solution containing sodium carbonate and sodium sulfide until the required amount of sodium bicarbonate has been added e. g. enough to convert the desired amount of sodium sulfide into a carbonate of sodium. The solutions will generally contain more sodium carbonate than sodium sulfide, for example two molecular proportions of sodium carbonate to one, more or less, of sodium sulfide. The amount of sodium bicarbonate added to such liquor is advantageously as much as, and preferably more than, called for by the assumed equation hereinbefore given for the conversion of all of the so-

dium sulfide into sodium carbonate with formation of hydrogen sulfide. The liquor may be treated advantageously below that temperature at which sodium bicarbonate or other acid carbonate present would be readily decomposed so as to cause escape of any considerable amount of gaseous carbon dioxide from the liquor; that is, the temperature should be, for example, below 60° C., say between 5° and 50° C. The concentrated and relatively cool liquor and solid sodium bicarbonate are admixed and agitated together and hydrogen sulfide formed and released from the liquor is withdrawn from the vessel, for example by means of a suitable suction pump or fan capable of reducing the pressure within the vessel to a considerable extent (e. g. a reduction of 6 to 8 inches of mercury, more or less) to aid in the removal of hydrogen sulfide from the liquid. The vessel should be of such a character that the liquid can be agitated and the vessel subjected to a suitably reduced pressure. The amount of hydrogen sulfide retained by the liquor after such treatment is less when the amount of liquor is relatively small and the gas pressure above it is relatively low; accordingly, the use of a relatively small amount of concentrated liquor and the use of a relatively high partial vacuum are advantageous. Vigorous agitation of such liquor also aids in removing hydrogen sulfide therefrom. With suitable temperature, vigorous agitation and low pressure, most, if not all, of the hydrogen sulfide can be readily removed, and the available carbon dioxide supplied, e. g. as sodium bicarbonate, can be utilized to good advantage.

It is possible, when the above treatment is of sufficient duration and intensity to effect a substantially complete removal of hydrogen sulfide, leaving little if any sulfide-sulfur in the solution. However, if a substantially complete removal of sulfide sulfur therefrom is not necessary or is even undesirable, the carbonating and related operations can be regulated to leave part of the sulfid-sulfur in the liquor. Ordinarily, and when a sulfite of sodium digesting liquor is to be produced, the greater part of the sulfide sulfur will be released and removed, and, in most cases, it will be more advantageous to remove all or nearly all of the sulfide sulfur, e. g. as hydrogen sulfide. The hydrogen sulfide, as pointed out above, may be burned in a combustion chamber connected to a sulfur burner and the resulting sulfur dioxide regained and employed in the production of sodium sulfite or an acid sulfite of sodium.

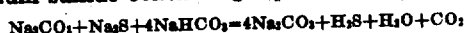
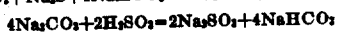
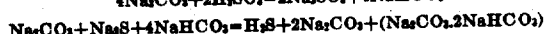
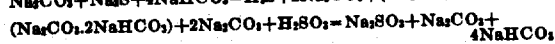
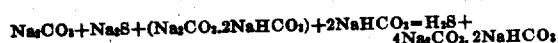
To aid further in the removal of hydrogen sulfide from the carbonated liquid, the liquid may be heated, for example after the major part of the hydrogen sulfide has been removed at moderate temperature. Such heating may be effected, for example, by a closed steam coil submerged in the liquid, and the liquid may be vigorously and continuously agitated either by mechanical means and/or a current of gases, such e. g. as carbon dioxide gases, passed through the liquid so as to expose a large surface thereof to the action of the gases.

In case the liquor which has been treated with a sodium acid carbonate still contains some sulfide sulfur, it may be treated with a suitable metallic compound, e. g., iron sulfate, so as to precipitate and remove the sulfide sulfur as an insoluble sulfide; also, the treated liquor may be subjected to a regulated and suitable oxidizing treatment such as will oxidize to the desired extent any residual sulfide sulfur, elementary sulfur

or/and thiosulfate, and thereafter the carbonate of sodium remaining with the liquor may be sulfited to the required degree in the regulated sulfiting treatment which is subsequently carried out.

After sulfide sulfur, etc., has been removed or disposed of by the procedure above described, the carbonate of sodium remaining with the liquor may be free from or substantially free from sulfur material such as will form or aid in forming an undesirable amount of sodium thiosulfate when the solution is subsequently sulfited to produce sodium sulfite and solid sodium acid carbonate.

Instead of using sodium bicarbonate in the carbonating step of the process, the available carbon dioxide may be supplied by other suitable carbonate which is capable of reacting with the sodium sulfide to form and release a volatile sulfide, such as hydrogen sulfide, etc. Thus, sodium compounds intermediate between the normal carbonate and bicarbonate may be used, as illustrated by the following equations, which illustrate the production of the bicarbonate and an intermediate carbonate as well as their reaction with sodium sulfide containing liquors.



In general, the smaller the volume of liquor employed for the carbonating treatment for a given amount of sodium sulfide the better and more readily the desired amount of volatile sulfide is eliminated. Accordingly, it is advantageous to use a concentrated solution of sodium carbonate and sodium sulfide in order to obtain better elimination of the desired amount of sulfide sulfur. The employment of sodium acid carbonate in solid form avoids undesired dilution of the solution and, if the solution is sufficiently concentrated, gives a slurry containing solid sodium carbonate at the end of the carbonating treatment. Such slurry can advantageously be sulfited and will give larger amounts of solid sodium acid carbonate upon the regulated sulfiting, than when much more dilute solutions are employed.

Although it is desirable, in making optimum utilization of the available carbon dioxide supplied for the treatment of the sodium sulfide, to have the sodium carbonate-sodium sulfide liquor below 60° C. when the liquor is treated with solid sodium acid carbonate, nevertheless a somewhat hotter liquor can be employed in cases where some loss of carbon dioxide as gas is unobjectionable, as where the available supply of solid sodium acid carbonate is much more than that required for forming and releasing the desired amount of volatile sulfide. In such case, for example, the solid sodium acid carbonate can be placed in the bottom of a fairly tall tank and a somewhat hotter sodium carbonate-sodium sulfide liquor poured on top of the solid sodium acid carbonate, care being exercised to insure that the liquor and the solids are well mixed beneath the surface of the liquor. The hydrogen sulfide released and removed may be delivered to the combustion chamber, e. g., of the sulfur burner. Some carbon dioxide may be lost as gas in this modified method of operation, and in this case, a sufficient excess

of the sodium acid carbonate should be employed to allow for such unutilized carbon dioxide.

Owing to the limited solubility of carbon dioxide in water or in aqueous solutions, an advantageous method to use when carbon dioxide is to be absorbed, e. g. from mixed gases containing it, is to produce a finely divided spray or atomization of a liquor which is to be treated with the carbon dioxide. The carbon dioxide is advantageously dissolved by the liquor while the gas is under pressure considerably greater than atmospheric. Ammonia may also be present in such gases. By spraying or atomizing such a liquor, e. g. a strong solution of sodium carbonate and sodium sulfide, into the carbon dioxide gases or into a mixture of gases which contains the carbon dioxide with or without ammonia, a very large amount of liquor surface is exposed to the gases and thus the absorption of the soluble gases is facilitated in an advantageous manner. If desired, the sprayed or atomized liquor and the gases (preferably under such increased pressure) can pass in opposite directions to each other, thus giving a counter-current effect. Enough available carbon dioxide should be supplied to the liquor to insure release and removal of the desired amount of sulfid sulfur.

Either after or during the absorption of the carbon dioxide a volatile sulfide may be removed from the liquor and the sulfur content of the volatile sulfide may be burned to produce sulfur dioxide. It is advisable to clarify the liquor before spraying or atomizing it and bringing the sprayed or atomized material into contact with the carbon dioxide-bearing gases. Air or other similar oxidizing gases are advantageously excluded from the gases while the volatile sulfide is being formed and released and while it is being removed, in case it is desired to avoid or minimize the formation of sodium thiosulfate in the liquor.

The carbon dioxide-bearing gases may be introduced into a suitable chamber at ordinary pressure or with advantage at a pressure considerably above that of atmosphere and the liquor sprayed or atomized into the chamber which contains such gases at pressure above atmospheric, to take advantage of the increased solubility of carbon dioxide under such pressure conditions. After the required amount of carbon dioxide has been absorbed in the liquor to convert the desired amount of sodium sulfide into a carbonate of sodium and to insure the elimination of the desired amount of sulfid-sulfur, it may be agitated and subjected to reduced pressure or/and heat, e. g. by spraying the carbonated liquor into a chamber which is maintained at a reduced pressure (e. g. below atmospheric pressure) by means of a suitable suction device or exhauster. And such liquor may be sprayed one or more times into such a chamber. The liquor may be heated, for instance, toward the end of its treatment in which a volatile sulfide is being removed therefrom, to facilitate removal of gaseous material.

From the foregoing it will be understood that CO<sub>2</sub> gas is not passed through the sodium carbonate-sodium sulfide liquor, as in the former methods disclosed by other parties, but on the contrary the available carbon dioxide, in the desired amount, is supplied to the sodium sulfide in the liquor and thereafter a volatile sulfide is removed from such a carbonated liquor by means of reduced pressure or/and heat, and agitation may advantageously be employed to facilitate removal of the volatile sulfide. Some or

all of the resulting carbonate of sodium can be thereafter sulfited under conditions to remove carbon dioxide in concentrated condition and this carbon dioxide, alone or in conjunction with ammonia, can be absorbed in liquor which contains a sulfide of an alkali metal, e. g. sodium sulfide.

In case a more direct treatment is desired, the sodium carbonate-sodium sulfide liquor may be boiled with enough lime to yield a liquor which contains a moderate amount of sodium hydroxide in addition to the sodium sulfide, together with a small or a moderate amount of sodium carbonate, and then the resulting liquor may be separated from the solids. This treatment may serve also to clarify the liquor and to remove iron compounds if any in the liquor. Such causticized liquor may be further concentrated if desired or necessary.

When the sodium sulfide-containing solution is first carbonated to release sulfide sulfur which is removed therefrom in the form of a volatile sulfide, the carbonated solution so produced and remaining may be subjected to a regulated sulfiting treatment for the production of a sodium acid carbonate and of a sulfite of sodium. The carbonate solution which is to be sulfited is advantageously a concentrated solution or a slurry containing an undissolved carbonate of sodium, since the sulfiting of such a solution or slurry results in the production of a solid sodium acid carbonate which can be separated from the liquor in considerable amount by filtration, centrifuging or otherwise.

In carrying out such a regulated sulfiting treatment, heat is generated by the reaction and, unless provision is made for getting rid of a sufficient amount of this heat, the temperature of the liquor may rise to an objectionable point such that resulting sodium acid carbonate would be decomposed or/and an insufficient amount of solid sodium acid carbonate would be precipitated. The sulfiting is therefore advantageously carried out in a vessel provided with cooling means for removing a desired amount of the thus generated heat. A cooling jacket or/and a cooling coil, together with agitation of the liquor and solids therein, can be employed for this purpose, this being particularly desirable when a concentrated sulfur dioxide gas is let into the liquor or sodium acid sulfite is added thereto. By proper regulation and using proper cooling coils, etc., a proper temperature can be maintained.

If the carbonate of sodium liquor, remaining after the carbonating treatment and the removal of sulfide sulfur, is too hot or/and too weak for the sulfiting treatment, such liquor can be cooled or/and concentrated before such treatment. It can be concentrated, for example, in a multiple effect evaporator to produce a suitably concentrated liquor such that upon subsequent cooling a considerable amount of a carbonate of sodium will separate out as a solid. During cooling of such concentrated liquor, it may be suitably agitated to insure the separation of finely divided particles of a carbonate of sodium, thus aiding in the subsequent treatment of the resulting slurry with sulfur dioxide or sodium acid sulfite. The unsulfited liquor can be cooled, if too hot, e. g. by showering the concentrated liquor into an open tower and causing a current of cold air with or without carbon dioxide gas to pass up through the tower in sufficient amount to cool the liquor. The liquor can be recirculated one or more times if desired, to effect further cooling. Such carbon

dioxide as may be absorbed from the gases and retained by the liquor, in case a carbon dioxide bearing gas is utilized during the cooling treatment, aids in the production of a sodium acid carbonate.

The strong and cool carbonate of sodium material (which is advantageously a mixture of a solid carbonate of sodium and a solution of a carbonate of sodium (a slurry) especially when the subsequent production of a relatively large amount of solid sodium acid carbonate, e. g.  $\text{NaHCO}_3$  is desired) is subjected to a regulated sulfiting operation, such as outlined above, by means of available sulfur dioxide supplied either as gaseous sulfur dioxide or/and as an acid sulfite of sodium, e. g.  $\text{NaHSO}_3$ , in strong and cool solution, or as a solid, or as a slurry.

The material which is being sulfited in the regulated sulfiting step is maintained (by suitable means) cool enough to retain all or at least most of the released or displaced carbon dioxide in the liquor or/and solids and to deposit an adequate amount of solid sodium acid carbonate for treatment of sodium sulfide. We have found that treatment of sodium sulfide is facilitated, in the cyclic process of the present invention particularly, by keeping carbon dioxide, which is to be used to react upon sodium sulfide, in or with the liquor or liquors of the process or, e. g. in the form of a solid carbonate of sodium and by avoiding the release of such an objectionable or prohibitive amount of such carbon dioxide as a gas, at least by thus retaining or conserving such  $\text{CO}_2$  to such extent as is required for the proper and desired treatment of the sodium sulfide to form and insure the release and removal of the desired amount of a volatile sulfide such as hydrogen sulfide. Thus the material being sulfited may be kept around a temperature of  $10^\circ$  to  $30^\circ \text{C.}$ , more or less; although moderately higher temperatures may be employed, especially when production of a relatively large amount of solid sodium acid carbonate is not required or desired.

In case sulfur dioxide for the regulated sulfiting step is supplied to the carbonate of sodium material in the form of a gas, e. g. such sulfur dioxide being derived from the combustion chamber in which hydrogen sulfide released from sodium sulfide is burned, such gas is advantageously cooled, if required, to a suitable point, e. g.  $10^\circ$  to  $20^\circ \text{C.}$ , more or less, in a suitable manner and then brought into suitable contact with the carbonate of sodium material to be sulfited, e. g. a slurry of solid carbonate of sodium with a liquor such as referred to above. The desired amount of sulfur dioxide may be absorbed to form the desired amount of sodium sulfite and of solid sodium acid carbonate, and the unabsorbed gases such as nitrogen, etc., which accompanied the sulfur dioxide gas from the combustion chamber, caused to pass on. Such unabsorbed and cooled gases aid in maintaining the temperature of the sodium compounds at a suitable point, as some of the heat generated by the reaction when a carbonate of sodium is sulfited is transferred to such relatively cool and unabsorbed gases and thus removed from the material being sulfited.

As stated above, the amount of carbonate of sodium sulfited should be regulated so that the desired amount of solid sodium acid carbonate is separated out or otherwise obtained, and then such sulfiting should ordinarily be discontinued, although more solid sodium acid carbonate than is required for the treatment of sodium sulfide can be produced by suitably regulating the oper-

ations. The material being sulfited is advantageously sufficiently cooled, by any suitable means, and suitably agitated while being sulfited so as to obtain rather uniform treatment and avoid an over-sulfiting of a portion of the carbonate of sodium material as a whole and an under-sulfiting of another portion, since an excessive over-sulfiting may cause an escape of gaseous carbon dioxide to an undesired extent, a result which usually should be avoided in case efficient and optimum use of carbon dioxide is sought. The following assumed equation may serve to illustrate the step when sulfur dioxide gas is used for regulated sulfiting.



An alternative method of sulfiting the sodium carbonate material in a regulated manner is to carefully admix a concentrated and cool solution of acid sodium sulfite with the sodium carbonate material, such as solid sodium carbonate or a slurry of sodium carbonate. The following assumed equation may serve to illustrate this alternative method.



The acid sodium sulfite can be obtained by absorbing cool sulfur dioxide gas, e. g. from the combustion chamber previously referred to above, in a regulated amount of concentrated and cool sodium sulfite solution. A slurry of solid sodium acid sulfite in a solution of sodium acid sulfite, or solid sodium acid sulfite alone, may be advantageously employed for the regulated sulfiting of the carbonate of sodium material, especially when production of a relatively large amount of solid sodium acid carbonate is desired.

Whichever method of subjecting the carbonate of sodium material to the regulated sulfiting treatment is employed, the solid sodium acid carbonate, e. g.  $\text{NaHCO}_3$ , may be separated from liquor which contains sodium sulfite, and as much of the liquor as practical removed from the solids in any suitable manner. A suitable centrifuge or a filter-press or even a reduced-pressure-filter of the rotary type may be employed when separating such liquor from such solids, and the solids may be treated to remove adhering liquor by any suitable method of washing, care being taken to avoid dissolving an excessive or prohibitive amount of the solid sodium acid carbonate during any such washing treatment. Some of the excess solid sodium acid carbonate, e. g. some excess solid sodium acid carbonate which has previously been washed to substantially free it from sodium sulfite, may be employed to make a cold saturated solution of sodium acid carbonate, e. g.  $\text{NaHCO}_3$ , and such solution may be used for washing another lot or batch of solid sodium acid carbonate to substantially free it from any objectionable amount, if any, of sodium sulfite adhering thereto.

The sodium sulfite liquor removed from the solid sodium acid carbonate, and especially the wash water, if any is produced, usually carries some carbonate of sodium in solution. Such liquor, with or without such wash water being admixed therewith, may be given a further sulfiting treatment, after its removal from the solid sodium acid carbonate, to convert such dissolved carbonate of sodium into a sulfite of sodium, and the sulfiting treatment may even be carried to such an extent that an acid liquor of the desired  $\text{SO}_2$  content and containing an acid sulfite of sodium is produced. Such liquor may be prepared in the

manner outlined, so that it carries little if any sodium thiosulfate and the amount of the latter can be regulated and controlled by exercising due care.

The sodium sulfite liquor, separated from the sodium acid carbonate solid material produced by the regulated sulfiting step, may be clarified in case this is needed or desirable. Should the sodium carbonate-sodium sulfide liquor, or a subsequent sodium carbonate containing liquor, contain an objectionable amount of iron-bearing material, e. g., as a finely divided iron carbonate or/and iron sulfide, such liquor may be boiled with a small or moderate amount of quick-lime sufficient to aid in clarifying the liquor and removing iron-bearing material therefrom, and the resulting liquor may thereafter be filtered or otherwise clarified in any suitable manner. Such amount of caustic soda as may be present in such a clarified liquor, e. g. a filtrate, in case it is to be carbonated thereafter by means of available carbon dioxide, should be allowed for and an adequate amount of available carbon dioxide supplied in addition to and over that theoretically required to decompose the desired amount of sodium sulfide.

When an excess of solid sodium acid carbonate, e. g.  $\text{NaHCO}_3$ , or  $(\text{Na}_2\text{CO}_3 \cdot 2\text{NaHCO}_3 \cdot 3\text{H}_2\text{O})$  the so-called sesqui-carbonate, is produced, i. e. more than is required for treating the sodium sulfide to release sulfid sulfur and form a carbonate of sodium therefrom, the solid material may be divided into two parts, e. g. the smaller part or excess being used to make a saturated or concentrated solution of such sodium acid carbonate in cool water and this solution suitably employed for economically washing another and larger lot of solid sodium acid carbonate to remove adhering liquor in which sodium sulfite is present in the dissolved state. The resulting washings, carrying some carbonate of sodium and some sulfite of sodium, may be sulfited to produce either normal sodium sulfite or/and an acid sulfite of sodium.

The solid sodium acid carbonate may be substantially, or to the desired extent, freed from adhering liquor (which contains sodium sulfite) by washing such solid material, for instance, by displacement of such adhering liquor by means of cold water, or by means of a cold solution of sodium acid carbonate (advantageously a concentrated solution), or by means of a cold solution of sodium carbonate (which may be a concentrated or a saturated solution), or by any other suitable means which will render and leave the washed solid sodium acid carbonate, e. g.  $\text{NaHCO}_3$ , substantially free from sodium sulfite and provide a sufficient amount of such washed solid sodium acid carbonate for the desired treatment of another lot of liquor which contains sodium sulfide, such as the sodium carbonate-sodium sulfide liquor referred to above, for example.

Such washing of the solid sodium acid carbonate to render it free or substantially free from sodium sulfite is important when an effort is being made to avoid the production of sodium thiosulfate or to minimize the amount of it produced, e. g. when treating a liquor containing sodium carbonate and sodium sulfide by means of the solid sodium acid carbonate produced by a regulated sulfiting treatment such as described.

When formation of a small or moderate amount of sodium thiosulfate in the liquor is not prohibitive or objectionable, the solid sodium acid car-

bonate need not be as carefully washed as when such thiosulfate formation is prohibitive or objectionable, and in such cases (i. e. where a small or moderate amount of such thiosulfate is less objectionable) the slurry of solid sodium acid carbonate and the liquor which contains the dissolved sodium sulfite can usually be separated sufficiently by means of a centrifuge or a good filter-press or a reduced-pressure-filter of the rotary type, provided the solid sodium acid carbonate is not subjected to a pressure so low or/and to such a high temperature as will decompose it and cause the escape of an objectionable or prohibitive amount of carbon dioxide as gas. Solid sodium bicarbonate is apparently more stable under reduced pressure than under high temperatures, however, so a reasonable and considerable reduction in pressure may be employed to aid in separating the liquor from the solids.

Some of the sodium sulfite liquor produced by the regulated sulfiting step, for example, may be kept cool and be employed (e. g. in a concentrated solution) to absorb  $\text{SO}_2$  gas to form an acid sulfite, e. g.  $\text{NaHSO}_3$ , and this acid sulfite of sodium may be employed for a regulated sulfiting treatment of a concentrated and cool sodium carbonate liquor or slurry to form solid sodium acid carbonate and leave sodium sulfite in the solution. Such sulfite of sodium as is not used in connection with such sulfiting treatment of a carbonate of sodium can be utilized in any suitable manner, for example it may be used in the production of a digesting liquor for digesting wood. The sodium acid sulfite employed for the regulated sulfiting treatment, in case this method of sulfiting is employed, may be in the form of a cold concentrated liquor or it may be in the form of a solid or of a mixture of liquor and solid, the higher concentrations permitting of the production of relatively larger amounts of solid sodium acid carbonate.

Where more sodium acid carbonate or/and sodium carbonate is produced in the operations than is required either for treating sodium sulfide or for forming a sulfite of sodium, e. g. ( $\text{Na}_2\text{SO}_3$ ), either compound, i. e. carbonate or acid carbonate, may be disposed of as may be advantageous to such extent as it may be available therefor. Thus washed and dried sodium bicarbonate, which may be provided of a rather high purity by a method outlined herein, may be produced and sold to such an extent that it is not needed in a subsequent operation of the process or methods.

In the treatment of a concentrated liquor which contains sodium carbonate and sodium sulfide, we have found it desirable, in some circumstances, to charge the concentrated liquor and admixed solid sodium acid carbonate (which has been added for the purpose stated) into a de-salting evaporator, e. g. a single-effect vacuum-pan heated by suitable means such as steam-heating piping, and connected to suitable cooling pressure-reducing devices such as a condenser and a suction-pump. By means of such equipment, the liquor can be heated and subjected to a reduced pressure at the same time, thus aiding in the removal of a volatile sulfide (e. g. hydrogen sulfide), and while the hydrogen sulfide is being removed the carbonate of sodium liquor may be undergoing concentration, and this concentration may be regulated so that a considerable amount of a solid carbonate of sodium may be deposited in the de-salter; and this solid carbonate of sodium may, if desired, be sepa-

rated from the residual or mother liquor in any suitable manner. The mother liquor, e. g. after such separation, may be sulfited in a regulated manner to produce a sulfite of sodium in solution and deposit a solid sodium acid carbonate, or the mother liquor together with all or a portion of the solid carbonate of sodium thrown down in the de-salting evaporator may be subjected to the regulated sulfiting step of the process. Such hydrogen sulfide as is removed from the de-salting evaporator and is not condensed, may be conducted to the combustion chamber of a sulfur burner and therein burned to form sulfur dioxide, e. g. after condensing some of the water vapor therewith.

Sulfur can be removed as a volatile sulfide, e. g. hydrogen sulfide, and a carbonate of sodium removed as a solid in the de-salter, in a continuous type of operation. Thus the sodium carbonate and sodium sulfide and the solid sodium acid carbonate may be fed into the de-salting evaporator in a continuous manner, and hydrogen sulfide and a solid carbonate of sodium removed more or less continuously therefrom. The mother liquor may build up in salts, e. g. sodium sulfate, and when the mother liquor has reached such a composition that it is advantageous to remove it from the de-salting evaporator, it may be removed and, for example, instead of sulfiting such mother liquor, it may in some cases be added to a residual liquor from a digesting step or steps of the process and sent to a furnace or furnaces to be so treated as to reduce sodium sulfate and form sodium sulfide thereby. Such mother liquor as is removed from the solid carbonate of sodium taken out of the de-salter, for instance by a centrifuge or by a filter, may be added to such other mother liquor as may be removed from the de-salting evaporator from time to time.

Solid carbonate of sodium removed from the de-salter may be disposed of in any suitable manner. Any surplus may be sold, or such carbonate of sodium may be subjected to a regulated sulfiting step to form a sulfite of sodium in part and a solid acid carbonate of sodium in part. The sulfite of sodium liquor produced in this manner, that is by obtaining a relatively pure carbonate of sodium in a solid state, separating it from mother liquor, and then sulfiting such carbonate of sodium in the presence of water, is less liable to be contaminated with sodium thiosulfate than when mother liquor containing sulfide-sulfur is sulfited; this being especially true when the de-salted carbonate of sodium is carefully washed by cold water or by a cold and concentrated or saturated solution of sodium carbonate prior to such de-salted carbonate of sodium being sulfited.

Having thus described in detail novel features of the process applicable to treatment of solutions produced by means of a step or steps of a regeneration process to produce cooking liquors for use in carrying out a pulp making process, we will now describe somewhat more in detail certain pulp making processes which are included in the novel cyclic or regenerative process. Certain of these pulp making processes in themselves as well as certain liquor treatment processes possess features of patentable novelty and are claimed herein.

In case the digesting treatment, e. g. of wood to produce chemical pulp, is carried out with an acid sodium sulfite liquor containing a large proportion of free sulfur dioxide, and in case some

sulfur dioxide gas is relieved from the digester during the cooking operation, or from the liquor or digester at the end of or subsequent to the cooking operation, this relieved sulfur dioxide may be cooled and employed for a regulated sulfiting of a carbonate of sodium as hereinbefore described; or such relieved sulfur dioxide may be used for sulfiting liquor resulting from a direct method of oxidizing sodium sulfide, as hereinbefore described. Alternatively, such relieved sulfur dioxide, or part of it, may be used to fortify a sulfite of sodium liquor to increase its content of sulfur dioxide either before or after such liquor is charged into a digester, or may be used to produce an acid sulfite of sodium and then to sulfite a carbonate of sodium.

When the regenerated cooking liquors contain some sodium thiosulfate, together with a rather large amount of sulfite as the main cooking reagent, the hydrogen ion concentration in the liquors appears to influence the tendency of loosely combined sulfur of the thiosulfate (i. e. one of the atoms of sulfur in sodium thiosulfate) to react with organic matter of wood or other cellulosic fibrous material, or of the liquor, with resulting production of darkened fibrous material which is unsuitable for some usages. Such darkened material is commercially unbleachable, in many cases. However, we have found that a small or moderate amount of sodium thiosulfate may be suitably employed in such regenerated cooking liquors, provided the hydrogen ion concentration therein is kept away from such a point or points as would favor an undesirable reaction of loosely combined sulfur of the sodium thiosulfate upon organic matter present.

An advantageous method of overcoming or counteracting the tendency of such loosely combined sulfur to produce such unsatisfactory fibrous material, is to employ in the liquor an amount of sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) in proportion to the weight of the raw fibrous material and of the non-fibrous organic matter therewith which is sufficiently large to prevent loosely combined sulfur being released from the thiosulfate and combining with organic matter to an objectionable degree, e. g. employing around 20% to 40%, more or less, of  $\text{Na}_2\text{SO}_3$ , based on the oven-dry weight of the wood. The sodium sulfite appears to exert a restraining or counteracting influence on such undesirable sulfur reactions and such restraining or counteracting influence is of practical commercial value when such sodium sulfite is present in adequate amount. A suitably limited and regulated amount of free or uncombined sulfur dioxide (i. e. that  $\text{SO}_2$  in excess of the amount theoretically required to form  $\text{Na}_2\text{SO}_3$  with the available and reactive sodium) may be employed, to facilitate the cooking operation, but an excessive or prohibitive amount of such free sulfur dioxide should be avoided, when thiosulfate is present, owing to its tendency to promote release of the loosely combined sulfur.

A cooking liquor containing sodium thiosulfate in regulated amount and considerably less in amount than the sodium sulfite present, which contains at least one molecule of sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) for each molecule of sodium acid sulfite ( $\text{NaHSO}_3$ ) has been found to be very useful in conjunction with the cyclic or regenerative process of the present invention, especially for cooking short-fibred woods to produce strong chemical pulp; and liquors ranging from equal molecules of sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) and bisulfite ( $\text{NaHSO}_3$ ) to liquors which con-

tain  $\text{Na}_2\text{SO}_3$  and little or no  $\text{NaHSO}_3$ , may be successfully used when they contain such a regulated and lesser amount of sodium thiosulfate. Just what function sodium thiosulfate has in such liquors is not clear, but it is known to possess reducing properties and, therefore, whatever advantage such an amount of sodium thiosulfate possesses is available in such regenerated cooking liquors. Sodium thiosulfate present in the resulting residual liquor is advantageous in a subsequent step as it can supply soda and sulfur to form  $\text{Na}_2\text{S}$ .

We give below certain examples illustrating the cooking of wood with certain and particular cooking liquors which may be advantageously employed in the cyclic or regenerative process of the present invention.

10,000 pounds of wood chips, e. g. of poplar wood or gum wood (oven-dry basis) may be digested by means of either one of the following liquors, using about 40,000 to 50,000 pounds, more or less, of such liquor. For example, the liquor may contain around 2,000 to 2,500 pounds of available or reactive sulfur dioxide, more or less, of which around 1,000 to 1,250 pounds, more or less, may be present as sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) and around 1,000 to 1,250 pounds, more or less, as sodium bisulfite ( $\text{NaHSO}_3$ ), and such liquor may also contain around 150 to 250 pounds, more or less, of sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ); or the liquor may contain around 2,000 to 2,500 pounds, more or less, of such sulfur dioxide of which around 1,250 to 1,500 pounds, more or less, may be present as sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) and around 750 to 1,000 pounds, more or less, as sodium bisulfite ( $\text{NaHSO}_3$ ), and such liquor may also contain around 200 to 500 pounds, more or less, of sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ). Other similar liquors, e. g. containing more sodium as sulfite ( $\text{Na}_2\text{SO}_3$ ) than as bisulfite ( $\text{NaHSO}_3$ ), may be employed, in each case having present in the liquor a considerable amount of available or reactive sulfite in excess of that actually required for the digesting reactions.

By keeping the amount of acid in the liquor down to a low point, as above shown, necessity for relieving sulfur dioxide gas from the digester during the cooking operation may be avoided or minimized so that recovery of sulfur dioxide from digester-relief gases is rendered unnecessary. Such mildly acid cooking liquor may be advantageously heated to a temperature considerably higher than is ordinarily used in the usual so-called acid-sulfite process, e. g. to a temperature around  $160$ – $180^\circ\text{C}$ ., more or less, and, owing to the relatively low acidity of the cooking liquor, strong and firm pulps and high yields may be obtained in relatively short time. This type of cooking liquor and cooking operation makes feasible the production of chemical pulps in good yield and of excellent quality from deciduous woods, as well as from non-deciduous woods. Moderately resinous pine wood, such as, e. g. jack pine, may be cooked by such liquors and good pulp produced, with little if any objection arising due to the resinous or pitchy content of such wood.

In case the cooking liquor contains considerably more sodium present as bisulfite ( $\text{NaHSO}_3$ ) than is present as normal sulfite ( $\text{Na}_2\text{SO}_3$ ), it is desirable to conduct the process (and particularly the regeneration steps) in such a manner that the cooking liquor is substantially free from, or contains at the most only a relatively small amount of sodium thiosulfate; and when either sodium bisulfite ( $\text{NaHSO}_3$ ) alone, or together with

free sulfurous acid ( $\text{H}_2\text{SO}_3$ ), is relied upon in the cooking liquor, it should preferably be almost, if not entirely, free from sodium thiosulfate.

When the cooking liquors contain a relatively large amount of free sulfur dioxide, the residual liquor from the digesting treatment of raw fibrous material therewith may be separated from the resulting fibrous material, then treated to remove water (and before removal of water therefrom the liquor may be neutralized or made alkaline to litmus, e. g. as hereinbefore described) and the solids, including carbonaceous matter, furnished in a suitable furnace under conditions adapted to form mostly sodium carbonate and sodium sulfide from the sodium compounds in the concentrated material. The resulting sodium carbonate and sodium sulfide can then be dissolved in water, e. g. to make a concentrated liquor, this sodium sulfide subjected to a regulated oxidation treatment (e. g. by forming a carbonate of sodium and a volatile sulfide, removing a volatile sulfide and oxidizing it to form sulfur dioxide and later combining such sulfur dioxide with a carbonate of sodium) and with such precautions as needed to avoid the formation of more than a relatively small amount, at the most, of sodium thiosulfate, and with such further sulfiting as needed so as to regenerate a sulfite of sodium cooking liquor of proper composition and strength, and this regenerated sulfite of sodium cooking liquor may thereafter be employed for a digestion of wood or other raw fibrous material for which it may be suited. Alternately, material which contains sodium sulfide or/and sodium thiosulfate (e. g. also containing an adequate and suitable amount of caustic soda) may be oxidized by means of gaseous oxygen, for instance, by spraying concentrated liquor containing such a sodium compound into air which has been heated to a suitable temperature.

When the cooking liquors employed have a relatively large amount of sodium sulfite ( $\text{Na}_2\text{SO}_3$ ), e. g. one having two or more molecules of  $\text{Na}_2\text{SO}_3$  for each molecule of  $\text{NaHSO}_3$ , it is advantageous to employ a relatively high cooking temperature. Thus good chips and such a cooking liquor may be charged into a digester, steam introduced into the lower portion of the digester in a manner to promote circulation of the cooking liquor therein, and with fairly uniform heating of the liquor through a period of, for example, around three hours, more or less, until a temperature of the cooking liquor of around  $160^\circ\text{--}185^\circ\text{C.}$ , more or less, has been reached. The liquor and fibrous material may be maintained approximately at such a relatively high temperature until the digestion has been carried to the desired degree. This may require a further period of around three to ten hours, more or less, relatively short periods usually being suitable for deciduous woods, while coniferous woods such as pines usually require a longer period than three hours for adequate digestion to produce chemical pulp suitable for bleaching.

Cooking liquors which are nearly neutral, or are mildly alkaline (to litmus), usually are milder in their action at a given temperature than those which have more acid ( $\text{SO}_2$ ) and hence the milder liquors should be given sufficient heating both as to temperature and time in order to produce the desired result. That is to say, with the milder liquors it is an advantage to employ temperatures higher than those temperatures which are usually suitable for use with liquors of relatively high acidity, i. e. containing relatively

large amounts of uncombined or free sulfur dioxide and relatively small amounts of combined  $\text{SO}_2$ . With relatively mild liquors, e. g. those which have as much soda in the form of  $\text{Na}_2\text{SO}_3$  as of  $\text{NaHSO}_3$ , and which mild liquors include the range all the way down in acidity to liquors which contain nearly all of the  $\text{SO}_2$  as  $\text{Na}_2\text{SO}_3$  and have only a small amount of  $\text{NaHSO}_3$  present therein, a great variety of woods may be digested to produce chemical pulps of such relatively high quality that they may be employed in relatively large proportions to produce papers of good quality.

Such mildly acid liquors are particularly suitable for the digestion of short-fibred woods (such as gums, poplars, birches, maples, etc.) to produce quality pulps. Such mild liquors are also well adapted to the digestion of some moderately resinous pines, which usually are unsuited for pulping with the conventional so-called acid-sulfite process employing a high free sulfur dioxide together with a calcium base, owing to their resin or pitch content. Such mildly acid sulfite of sodium liquors may, if desired, contain small to moderate amounts of sodium thiosulfate, but the amount of such thiosulfate should be kept below that which is liable to produce a darkened stock such as is commercially unbleachable. In general, the greater the percentage of  $\text{SO}_2$  as compared to sodium sulfite in such acid liquors, the lower the amount of thiosulfate which can be employed in such liquors.

The residual liquors from such digestion operations with such mild sulfite-bearing liquors may be treated by processes of the present invention so as to regenerate digesting liquors of the same kind or of a different kind. Likewise, residual liquors from digestion operations with liquors which contain a relatively high proportion of free or uncombined sulfur dioxide may be treated by processes of the present invention to regenerate digesting liquors of the same kind or of a different kind; and sulfur thereof can be regained and used in the form of sodium sulfide as pointed out herein.

Residual liquor from a digesting operation in which the principal digesting reagent is a sulfite, either with or without previous concentration, and either with or without having had alkaline compounds (e. g. sodium compounds) added thereto, may be (for example) introduced into the upper portion of a suitable scrubbing tower and subjected therein to the action of a current of gases derived from a furnace in which the reducing furnace treatment is conducted, the liquor flowing over checker-work in the tower from top to bottom and the gases ascending through the checker-work. When such gases are sufficiently hot, and when they carry some sodium compounds, the liquor may become more concentrated in sodium compounds during its descent through the tower; and if the gases carry some available sulfur trioxide, e. g. as sulfuric acid or as sodium sulfate, such liquor usually absorbs some of it. When such gases carry a large amount of an uncombined acid which is capable of displacing sulfur dioxide from sodium sulfite, the gases beyond such scrubbing tower may carry a considerable amount of sulfur dioxide, especially when the residual liquor charged into the upper portion of such a tower is acid to litmus and contains a considerable amount of an acid sulfite of sodium.

When such effluent gases from such scrubbing tower or chamber are scrubbed with a carbonate

of sodium liquor, for example, or with a cool solution of sodium sulfite, some sulfur dioxide can be regained from such gases for reuse. Some residual liquor, either with or without having been passed over such a scrubbing tower, one or more times, may be sprayed or atomized into suitable hot gases (for example hot gases derived from the reducing furnace and after oxidation to form sulfur dioxide, and just after such hot gases have been passed through a steam boiler) while such gases are passing through a suitable spray chamber, the spraying or atomizing being carried out under such conditions that a considerable amount or substantially all of the water content of the sprayed or atomized material is removed by evaporation and so that a highly concentrated liquor or a dry powdered material, as the case may be, is produced thereby.

Such spraying or atomizing may be in one operation, or the liquor may first be sprayed into hot gases to produce a concentrated liquor and the latter thereafter sprayed or atomized into such hot gases and converted into a powdered sodium-organic product. When producing such powdered material, the gases may be passed through an electrical precipitator, which may be placed beyond the spray chamber, if desired, to collect such dried material as may not have previously settled out from the gases. A scrubbing tower or chamber may be operated beyond such electrical precipitator and, for example, may be fed with a carbonate of sodium liquor so as to absorb sulfur dioxide, etc. from the gases when present therein.

When an acid residual liquor is sprayed or atomized in the manner disclosed, the gases beyond the spray chamber or/and electrical precipitator may carry a relatively large amount of sulfur dioxide which can be regained as pointed out.

In the treatment of the sprayed or atomized residual liquor by means of hot furnace gases, care should be taken to avoid over-heating and consequent carbonization of an undesired or objectionable amount of sodium-organic material derived from the digesting operation, especially when the resulting powdered sodium-organic material is to be used as fuel, e. g. as powdered fuel in the furnace, and the furnacing operation is to be carried out under such reducing conditions that a relatively large amount of sodium sulfide is to be obtained in the furnace product, especially when the hot products of combustion of such powdered fuel are to be used in a boiler for the production of steam.

When such hot products of combustion are passed through a boiler, some solids may be thereby collected; and these may be added to the concentrated liquor or to the powdered carbonaceous material which is to be burned in the furnace. The arrangement may be such that the furnace gases pass through a combustion chamber, then through a boiler, then through a spray chamber (with or without an electrical precipitator), then through a scrubber, and then to atmosphere. Each of these devices may have one or more sections either in parallel or in series, as may be desirable, and one or more suitable liquors may be used in the spray chambers, towers, etc. Electrical precipitators may be employed with or may be placed after a spray chamber or chambers so as to collect either solids or liquids or both. By evaporating substantially all of the water of the residual liquor by means of hot gases acting upon sprayed or atomized liquor beyond the boiler,

thus getting a dry fuel, and using this dry fuel in the furnace before the steam boiler, a relatively large amount of steam can be generated therein. Some of the organic material of the residual liquor can be destructively distilled or carbonized by the hot gases in the spray chamber, if desired, and combustibles in the residue may be thereafter burned, e. g. under reducing conditions to form  $\text{Na}_2\text{S}$ .

By burning substantially dry sodium-bearing organic material in the reducing furnace, instead of using a concentrated liquor in the furnace, the hot products of combustion beyond the combustion chamber have a relatively greater amount of available heat, and such available heat can be utilized to advantage in producing steam in the boiler, owing to the relatively high flame-temperatures and to the relatively smaller amount of highly heated water vapor in such products of combustion. The furnacing operation may be advantageously so conducted that the sodium compounds derived from residual liquor, to a large extent, are deposited in the lower regions of the furnace, together with sufficient incandescent carbon to insure any sodium-oxy-sulfur compounds present being reduced to the desired degree and extent, i. e. so that a relatively large amount of  $\text{Na}_2\text{S}$  is formed together with sodium carbonate.

Sulfur dioxide, if any, contained in the relatively cool gases after they have passed beyond the spray evaporator or/and driers, and beyond the relatively hot scrubbing tower or towers, if any are employed, can with advantage be regained by scrubbing such gases with a cool sodium sulfite liquor (to form an acid sodium sulfite liquor which can be used, e. g. for cooking raw fibrous material or for a regulated sulfiting treatment of a carbonate of sodium) or by scrubbing the gases with a carbonate of sodium liquor to form a desired amount of a sulfite of sodium therein. Such a carbonate of sodium liquor, when so used, is preferably substantially free from sodium sulfide and may be obtained, for instance, from the product resulting from treatment of sodium carbonate and sodium sulfide to remove sulfide-sulfur therefrom, either by forming and removing a volatile sulfide or by an oxidizing treatment of sodium sulfide, e. g. to produce sodium sulfite directly. Thus solid sodium carbonate, in whole or in part, or/and mother liquor, present after concentrating and cooling a substantially sulfide-free sodium carbonate liquor, may be employed for recovering sulfur dioxide from furnace gases, e. g. those beyond the spray chambers or/and relatively hot scrubbing towers in which residual liquor or liquors are treated by the furnace gases, preferably such as carry sulfur dioxide. Such sulfur-dioxide bearing gases may be derived, at least in part, by burning combustible gases, under regulated oxidizing conditions, derived from a furnace in which sodium-organic materials, from residual liquor resulting from cooking wood with an  $\text{NaOH-Na}_2\text{S}$  liquor, are calcined or/and carbon burned.

Sodium carbonate and sodium sulfide resulting from the reducing furnace treatment, e. g. in the form of a melt or smelt, may be dissolved in water in a suitable tank or dissolver provided with an agitator and with a suitable coil of iron piping, and a cool neutral or alkaline sodium sulfite liquor may be passed inside of this piping so as to obtain a preheating of such sodium sulfite liquor by absorbing heat from the hot sodium carbonate-sodium sulfide liquor in the tank or

dissolver. In case it is desired to cool the latter liquor to down below 60° C., for example, cool water or other cool liquid in adequate amount and of sufficiently low temperature may be passed through this piping to effect the desired degree of cooling of the liquor in the dissolver.

The processes of the present invention make feasible the operation of a pulp-mill or pulp-mills with one type of digesting liquor alone (employing a sulfite of sodium therein) or with more than one type of digesting liquor; that is, it may be a "single-liquor mill" or a "multiple-liquor mill". For example, a digestion of wood may be effected by means of a cooking liquor which contains mostly sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) as the digesting reagent, and with but little or no sodium thiosulfate present in such digesting liquor. The resulting residual liquor may be separated from the resulting fibrous material, then suitably cooled, and enough sulfur dioxide absorbed therein or/and sodium bisulfite added thereto to produce a moderately acid cooking liquor which contains the desired amounts of free and of combined  $\text{SO}_2$ , and this acid cooking liquor then employed for a digestion of wood (etc.). The excess sodium sulfite ( $\text{Na}_2\text{SO}_3$ ), i. e. that which was not consumed in the first digestion treatment, remaining in the first residual liquor serves to supply soda and combined sulfur dioxide for the acid sodium sulfite cooking liquor made in this manner. Then an acid sodium sulfite cooking liquor digestion (e. g. of wood) is carried out, the second resulting residual liquor separated from the resulting fibrous matter, and such latter residual liquor (together with wash waters if desired and with or without addition of alkaline material thereto) subjected to a concentrating treatment and the solids thereafter furnaced under strongly reducing conditions adapted to form mostly sodium carbonate and a relatively large amount of sodium sulfide from the sodium compounds. These two compounds ( $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{S}$ ) are dissolved in water to form a liquor, this liquor is causticized to form an alkaline digesting liquor which contains caustic soda (advantageously in preponderating amount) and sodium sulfide as its sole or as its principal digesting reagents, and such alkaline cooking liquor is employed to digest wood, etc., e. g. to form chemical pulp, and to form an alkaline sulfur-bearing residual liquor. The latter residual liquor may then be concentrated and the solids furnaced to convert most of the sodium compounds into sodium carbonate, the latter being either free from or accompanied by but a small amount of sodium sulfide. These two materials may then be subjected to a regulated and controlled oxidation treatment, either direct or indirect or both, in accordance with the processes outlined in this specification, and the soda treated to form a sulfite of sodium cooking liquor which may either be free from free sulfur dioxide or contain such an amount thereof as will render the resulting liquor suitable for the digestion of wood to produce chemical pulp thereby. Sodium thiosulfate will be present in only small quantity, if any, in such sulfite of sodium cooking liquor. Such an operation is for a "three-or-more-liquors mill".

An alternative method of operating, in a "two-liquor mill", for example, is to carry out a digestion treatment on wood (or other suitable cellulosic-fibrous material) by means of a suitable cooking liquor which contains a sulfite of sodium (such cooking liquor may or may not contain some normal sodium sulfite; and it may or may

not contain some sodium bisulfite; and it may or may not contain any additional sulfur dioxide beyond the sodium bisulfite stage) until such raw material is digested to the desired degree, e. g. until chemical pulp is obtained. The resulting residual liquor may thereafter be concentrated either with or without rendering it neutral or alkaline (e. g. by adding alkaline soda material thereto, such as a mixture of sodium carbonate and sodium sulfide derived from a reducing furnace treatment of solids from a suitable residual liquor) and the solids furnaced under strongly reducing conditions to form sodium carbonate and a relatively large amount of sodium sulfide, these compounds thereafter being dissolved and sodium carbonate in the resulting liquor causticized by means of lime to form a cooking liquor containing caustic soda (e. g. in preponderating amount) and sodium sulfide.

Such latter cooking liquor is then employed for a digestion treatment to produce pulpy material from wood, etc. (e. g. chemical pulp) and the resulting residual liquor treated by a process or processes of the present invention to eliminate organic matter and to produce a sulfite of sodium cooking liquor suitable for digesting wood to produce chemical pulp (and with a regulated amount of thiosulfate or free therefrom) and the latter liquor then employed for such a digestion treatment. The reproduced digesting liquor may be an acid sulfite of sodium liquor such as was first employed or it may be of a different composition so long as it is suitable for the operation to which it is to be put. In such a two-liquor mill operation, the amount of thiosulfate in the sulfite-type of cooking liquor can be kept very low or absent.

In such a "two-liquor mill" operation sulfur is employed in a sulfite of sodium cooking liquor, then some of the same sulfur is used in a liquor which contains sodium sulfide and some of the sulfur may then be regained and reused in the reformed or regenerated digesting liquor which contains a sulfite of sodium. Some of the same sodium is employed in each of the two digesting liquors. A sulfate of sodium may be employed for replacing lost soda and some of the sulfur losses in the operations; or a carbonate of sodium or sodium hydroxide may be employed to replace lost soda; or a sulfate of sodium and a carbonate of sodium or/and sodium hydroxide may be employed to replace some material lost in the operations. Sulfur may be dissolved in caustic liquor to form some sodium sulfide and some oxysulfur material, and such use of sulfur may be resorted to as to enhance the sulfidity of the caustic liquor or/and as an aid in maintaining a desired ratio of  $\text{NaOH}$  to  $\text{Na}_2\text{S}$  fairly constant even when other conditions might tend to result in non-uniformity.

It will thus be seen that the present invention presents improvements in the cooking of wood, etc., e. g. for the production of chemical pulp, in regenerative, cyclic or/and inter-related processes therefor, in the treatment of residual liquors, in the production of cooking liquors, and in individual steps of the process which involve the production of sodium carbonate from sodium sulfide by a novel carbonating treatment, and the production of a sodium acid carbonate by a regulated sulfiting of a carbonate of sodium.

Liquors obtained by dissolving sodium compounds, including sodium carbonate and sodium sulfide, contained in the furnace product derived from residual liquor from a digesting operation

employing cooking liquor supplied with a sulfur-bearing compound of sodium, e. g. a sulfite, may vary considerably in proportions of the various constituents. In particular the ratio of sodium carbonate to sodium sulfide may vary throughout a fairly wide range. When the amount of sodium sulfide is relatively high, e. g. when the amount of sodium present as sodium sulfide is approximately as large as the amount of sodium present as sodium carbonate, it is somewhat more difficult to treat the recovered sodium compounds to form a cooking liquor which contains the desired amount of a sulfite of sodium and little if any sodium thiosulfate, then it is when the amount of sodium carbonate in the furnace product is very much larger than the amount of sodium sulfide therein. In the latter case there is more carbonate radicle available for providing the available carbon dioxide, e. g. upon the regulated sulfiting of a carbonate of sodium by means of  $\text{SO}_2$ , to the sodium sulfide so as to form a volatile sulfide, e. g. as an acid carbonate of sodium, than when the amount of sodium sulfide in the furnace product is relatively high.

Therefore, there are some advantages in using a multiple-liquor mill, e. g. a two-liquors pulp mill so operated as to employ sulfur in one instance primarily as a sulfite and in another instance as a sulfide. For example, by cooking wood with an acid sulfite of sodium cooking liquor, either free from or with a suitable amount of sodium thiosulfate or/and sodium sulfate, to produce chemical pulp, separating resulting residual liquor from resulting fibrous material, removing water from such liquor, furnacing resulting solids under strongly reducing conditions adapted to yield a furnace product which contains mostly sodium carbonate and sodium sulfide, with the latter being relatively high in amount, an advantage is obtained by causticizing the sodium carbonate and forming a cooking liquor which contains sodium hydroxide and a relatively large amount of sodium sulfide (and which cooking liquor may or may not contain some sodium sulfite, or sodium thiosulfate, or both, in moderate amount), and employing such strongly alkaline cooking liquor to cook wood to produce chemical pulp and to form sodium-organic compounds including most of the sodium content of both the sodium hydroxide and the sodium sulfide, and to heat solids derived from residual liquor resulting from such strongly alkaline cook to destroy organic matter and obtain a furnace product which contains most of its soda content in the form of sodium carbonate (and free from or with a relatively smaller or lesser amount of sodium sulfide), and then sulfiting such sodium carbonate either without or after oxidizing or forming a volatile sulfid for the production of a sulfite of sodium and employing it in cooking liquor which is to have at the most only a small amount of sodium thiosulfate. Such an operation is advantageous and especially desirable when the sulfite of sodium cooking liquor so produced is to have a relatively large amount of  $\text{SO}_2$  over and above that required for forming normal sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) with the available soda.

The alkaline cooking liquor utilized in such a cycle preferably contains sodium hydroxide in greater amount than sodium sulfide and may also contain or be free from other chemicals in moderate amounts such as sodium sulfite, sodium thiosulfate, sodium carbonate, sodium sulfate, etc.

In some instances, black liquor of the type described above resulting from a production of pulp

with a strongly alkaline cooking liquor may be sulfited directly so as to convert reactive sodium compounds thereof into a sulfite of sodium, precipitating organic matter, separating the sulfited liquor from the precipitated organic matter and thereafter employing the directly sulfited liquor, either with or without further modification as may be necessary or desirable (e. g. by dissolving more sulfur dioxide therein to increase its content of  $\text{SO}_2$ ), for a digesting operation of fibrous material to produce pulp. Such direct sulfiting of the black liquor may be carried out by dissolving  $\text{SO}_2$  gas therein, or/and by adding sodium acid sulfite thereto, advantageously adding enough  $\text{SO}_2$  so that the liquor is rendered acid to litmus and so that most of the precipitable organic matter is precipitated; and such precipitated organic matter may be removed from the liquor in any suitable manner. The organic matter so removed may be furnaced advantageously along with solids derived from residual liquor resulting from a sulfite of sodium type cooking operation. The organic matter thus returned furnishes carbonaceous matter to assist in carrying out a strongly reducing furnace treatment by which are produced sodium carbonate and a relatively large amount of sodium sulfide. Any soda which is contained in the precipitated organic material may thus be added to the soda of residual liquor from a sulfite of sodium type of digestion operation.

When all of such black liquor is thus subjected to a direct sulfiting treatment and the complete cycle is carried out in the manner indicated, it will be seen that only one furnacing operation is employed although two cooking operations are carried out. This method therefore secures a more efficient utilization of sulfur and soda, since there is less danger of losing soda, or rather the amount lost may be reduced and some of the sulfur and soda constituents of the black liquor, which would ordinarily be lost during an additional furnacing treatment, are retained in the liquor when it is directly sulfited. The retained sulfur and soda in such case will be present in the sulfite of sodium type of cooking liquor and become available for the production of sulfide-sulfur when a residual liquor resulting therefrom is furnaced under reducing conditions. When such direct sulfiting of black liquor is practiced, the sulfite of sodium type of cooking liquor will usually carry some thio compound, e. g. sodium thiosulfate, and therefore the sulfite of sodium type of cooking liquor should carry enough sulfite combined as sodium sulfite to overcome the tendency of any such thio-compound or compounds to injure the fibres, e. g. by darkening them to a prohibitive degree, as previously pointed out. Thus liquors in which at least as much  $\text{SO}_2$  is present as normal sodium sulfite as is present as sodium bisulfite may be produced in this manner and employed to digest wood. The amount of thio-material therein will be in most, if not all, cases low enough for such liquors to be satisfactorily used and satisfactory pulp be thereby obtained.

In case the operator does not choose to directly sulfit all of the black liquor as described in the preceding paragraphs, any desired portion of such black liquor may be chosen and directly sulfited. Any remaining portion of the black liquor may be treated to remove remaining water therefrom and the resulting solids furnaced under, e. g. reducing conditions to produce sodium carbonate and sodium sulfid, the former usually being in preponderating amount. Such sodium compounds may be dissolved in water and the re-

sulfiting solution causticized to form a sodium  
 hydroxide-sodium sulfide cooking liquor of the  
 type previously referred to in this paragraph and  
 such cooking liquor may be employed to produce  
 5 pulp. Instead of causticizing such sodium car-  
 bonate-sodium sulfide liquor, a portion or all of it  
 may be treated to produce a sulfite of sodium type  
 of cooking liquor and the latter employed to pro-  
 10 duce pulp. The black liquor, or any desired por-  
 tion of it, may be treated so as to furnace the  
 solids thereof under either oxidizing or advan-  
 tageously under reducing conditions, the latter  
 being especially desirable when the sodium car-  
 15 bonate and sodium sulfide in the furnace product  
 are to be employed to produce a sodium hydroxide-  
 sodium sulfide type of cooking liquor; and such  
 black liquor, or the desired portion thereof, may  
 be treated separately or in conjunction with solids  
 20 derived from residual liquor from the sulfite of  
 sodium type of cooking liquor, by subjecting the  
 liquor with or without admixed solids to a  
 strongly reducing treatment to form sodium car-  
 bonate and sodium sulfide. Thus a cyclic process  
 25 may be used in which black liquor may be directly  
 sulfited to form a cooking liquor containing some  
 $\text{SO}_2$  over and above the amount needed to form  
 normal sodium sulfite with the available soda,  
 wood may be cooked therewith, the resulting re-  
 30 sidual liquor may be admixed with more black  
 liquor and the admixture treated under suitable  
 conditions to form sodium carbonate and sodium  
 sulfide; this sodium carbonate may be subjected  
 to a causticizing step and the resulting sodium  
 35 hydroxide and the sodium sulfide may be em-  
 ployed to cook wood, etc. to produce pulp. In  
 one respect, such a process may be considered as  
 a means for supplying sodium sulfide to an alka-  
 line cooking liquor by first using the sulfur as a  
 40 sulfite and later as a sulfide, and the amount of  
 sulfur thus supplied may be regulated so that the  
 sodium sulfide content of the alkaline cooking  
 liquor can be kept fairly constant if desired.  
 Sodium sulfate, or bisulfate, or both may be em-  
 45 ployed to replace soda lost in the operations; or  
 sodium hydroxide or/and sodium carbonate may  
 be employed for such purpose, the hydroxide  
 usually being supplied to the alkaline cooking  
 50 liquor and the sodium carbonate being advan-  
 tageously employed to form a sulfite of sodium  
 for the other type of cooking operation. In case  
 it is desired to produce more pulp by the alkaline  
 cooking liquor than usual and the sodium sulfide  
 55 content of the alkaline cooking liquor becomes  
 or tends to become too low for the best and most  
 uniform results, elementary sulfur in right  
 amount can be dissolved in the alkaline liquor  
 before, during or after causticizing sodium car-  
 60 bonate, this procedure forming some sulfide of  
 sodium and some trioxysulfur material such as  
 sodium thiosulfate. The latter may be converted,  
 at least in part, into sodium sulfite and sodium  
 sulfide by heating the solution of sodium hy-  
 65 droxide, sodium sulfide and sodium thiosulfate  
 under pressure to a high temperature for a suf-  
 ficient period of time, e. g., heating up to around  
 180 to 200 degrees C. for a period of two or three  
 hours, more or less, and apparently causing  
 70 sodium hydroxide to react with one of the sulfur  
 atoms of the sodium thiosulfate to form sodium  
 sulfide and sodium sulfite.

The processes of the present invention make  
 feasible the cooking of short-fibred woods, such  
 as poplars, gums, maples, birches, etc. by an ad-  
 75 vantageous acid sulfite of sodium type of cooking

liquor under conditions adapted to produce a  
 relatively high yield of chemical pulp of good  
 strength and possessing good bleaching qualities,  
 and such cooking liquor may contain an amount  
 of  $\text{SO}_2$  which provides a mixture of sodium sul-  
 5 fite and sodium bisulfite, with the former con-  
 taining as much as or more  $\text{SO}_2$  than is contained  
 in the bisulfite, for example, and care being  
 taken to digest the wood to such a degree that it  
 yields a chemical pulp of good bleaching qualities  
 10 and which bleached pulp contains fibres of ample  
 strength and felting properties that it can be em-  
 ployed in relatively large amount, for example,  
 a preponderating amount, in the manufacture of  
 papers known as book papers and magazine pa-  
 15 pers, as well as writing papers, etc. Resinous  
 pines which are generally considered unsuited to  
 pulping by the conventional so-called acid sulfite  
 process employing calcium base, may be suitably  
 20 pulped by the alkaline cooking liquor containing  
 a preponderating amount of sodium hydroxide  
 and a lesser amount of sodium sulfide, such as  
 described above. And when a moderate amount  
 of sodium sulfite is employed in such alkaline  
 cooking liquor for digesting such resinous pine  
 25 woods, the chemical pulp thus produced may be  
 bleached to a fairly high white such that the  
 bleached pulp containing the long fibres, can be  
 employed in admixture with the short fibred  
 bleached pulp produced by the special acid sulfite  
 30 type of cooking operation, to make the kinds of  
 papers mentioned. This arrangement, which is  
 just the opposite of that which has heretofore  
 been customarily employed (e. g. pulping spruce,  
 etc. by the conventional acid-sulfite process to  
 35 produce the long fibred stock, and pulping the  
 short-fibred woods, such as poplar, by a sodium  
 hydroxide cooking liquor, and employing these  
 two pulps to produce such papers), is of especial  
 utility in producing such papers from woods  
 40 grown in the southern portions of the United  
 States, for example, since a number of the more  
 readily available short-fibred woods of such  
 southern region do not usually yield chemical  
 pulps which are readily bleachable to a high  
 45 white when cooked by the conventional soda  
 process, and since the long-fibred woods, such as  
 the pines, of such region are not ordinarily con-  
 sidered to be available for pulp-making purposes  
 by the conventional acid sulfite process. By re-  
 50 versing the customary arrangement, i. e. pulping  
 the short-fibred woods by means of a cooking  
 liquor employing the sulfite radicle as an active  
 digesting agent, e. g. as an acid sulfite of sodium  
 cooking liquor of suitable composition, and pulp-  
 55 ing the resinous woods by means of an alkaline  
 liquor such as described above, book papers, mag-  
 azine papers and writing papers of good quality  
 can be readily obtained in an economical man-  
 ner. The short-fibred pulps obtained by such  
 60 special acid sulfite of sodium cooking liquors may  
 be varied considerably by changing the ratio of  
 combined  $\text{SO}_2$  to uncombined  $\text{SO}_2$  (e. g.  $\text{Na}_2\text{SO}_3$   
 to  $\text{NaHSO}_3$ ) and by varying the amount of chem-  
 65 icals, time and temperature of treatment, etc.  
 Such pulps may be obtained so that they are suf-  
 ficiently hard to be suitable for writing-papers, or  
 soft enough to be employed in large amount in  
 the other types of papers, especially when the  
 amount of normal sodium sulfite is rather large  
 70 as compared with the amount of sodium bisul-  
 fite. Such short-fibred pulps are new and differ-  
 ent pulps from those heretofore obtained from  
 such woods by the conventional acid-sulfite-pro-  
 cess and the papers made by the use of, for ex-  
 75

ample, a preponderating amount of such short fibres are also new and different papers; as well as such papers when they comprise some long-fibred pulps derived from such resinous pines in the manner described; and the cyclic operation is new and novel and has particular advantages as pointed out.

The process or processes of the present invention are capable of numerous variations and modifications without departing from the spirit of the invention.

In the claims the term "black liquor" is intended to include any residual liquor resulting from a digesting treatment of raw cellulosic-fibre-bearing material with a cooking liquor that contains a sodium compound as a digesting reagent.

We claim:—

1. A method of producing solid sodium bicarbonate and a solution containing sodium sulfite and sodium bicarbonate which comprises treating a solution containing sodium sulfid with available carbon dioxide in amount not materially exceeding the amount required to convert sodium sulfid into carbonate of sodium, heating the solution to drive out the resulting hydrogen sulfid from the solution, cooling the solution to a temperature below 60° C., sulfiting the resulting solution with an amount of available sulfur dioxide not materially exceeding the amount required to convert all of the carbon dioxide of the carbonate of sodium into sodium bicarbonate, maintaining a concentration of the solution such that solid sodium bicarbonate is precipitated, and separating the resulting precipitated sodium bicarbonate from the sodium sulfite solution.

2. The method of producing solid sodium bicarbonate and sodium sulfite in solution which comprises treating a solution of sodium sulfide at a temperature above 60° C. with solid sodium bicarbonate in amount sufficient to release substantially all the sulfide-sulfur as hydrogen sulfide and to convert the sodium sulfide into sodium carbonate, removing the hydrogen sulfide from the solution, cooling the resulting sodium carbonate solution to a temperature below 60° C., sulfiting the resulting cooled sodium carbonate solution until substantially all the carbon dioxide is combined as sodium bicarbonate, said solution being sufficiently concentrated so that a preponderating portion of the sodium bicarbonate is precipitated from the resulting solution of sodium sulfite.

3. A method of producing solid sodium bicarbonate and sodium sulfite in solution which comprises treating a solution containing sodium carbonate and sodium sulfide with solid sodium bicarbonate at a temperature in excess of 60° C., removing hydrogen sulfide from the hot solution, oxidizing the hydrogen sulfide to produce sulfur dioxide, cooling the treated solution, sulfiting the solution at a temperature below 60° C., and during agitation thereof until substantially all the carbon dioxide is combined as sodium bicarbonate, and a preponderating portion of the sodium bicarbonate is precipitated, and separating precipitated sodium bicarbonate from the sodium sulfite solution.

4. The method of producing sodium sulfite in solution and solid sodium bicarbonate which comprises subjecting a carbonate of sodium in solution to a sulfiting treatment at a temperature below 60° C. during agitation of the solution and discontinuing the sulfiting treatment when substantially all the carbon dioxide is combined as sodium bicarbonate, the temperature of the solu-

tion and the ratio of water to carbonate of sodium in the solution being so regulated that a preponderating portion of the resulting sodium bicarbonate separates out therefrom as solid sodium bicarbonate, and separating the solid sodium bicarbonate from the resulting solution.

5. The method of producing alkali sulfite and alkali bicarbonate which comprises subjecting a solution of alkali carbonate to a sulfiting treatment until substantially all the carbon dioxide of the alkali carbonate is combined as alkali bicarbonate, and regulating the sulfiting treatment by maintaining the temperature of the solution below 60° C. and by agitating the solution while introducing available sulfur dioxide therinto so as to substantially prevent the release of free carbon dioxide from the solution.

6. The method of obtaining a sodium sulfite solution and solid sodium bicarbonate which comprises subjecting a solution containing sodium carbonate to a sulfiting treatment at a temperature below 60° C. until substantially all of the carbon dioxide content of the sodium carbonate is combined as sodium bicarbonate and some of the sodium bicarbonate is precipitated from the solution, and separating a solution of sodium sulfite from the resulting solid sodium bicarbonate.

7. The cyclic process of converting sodium sulfide into sodium sulfite which comprises treating a solution of the sodium sulfide with sodium bicarbonate, removing from the solution hydrogen sulfide formed therein, burning the hydrogen sulfide to form sulfur dioxide, cooling the solution to a temperature below 60° C. treating the cooled solution with the sulfur dioxide so formed, the temperature of the solution being maintained low enough and the ratio of sodium bicarbonate to water being so regulated that solid sodium bicarbonate separates out from the solution separating solid sodium bicarbonate from the resulting sodium sulfite solution, and utilizing the solid sodium bicarbonate for treating further amounts of sodium sulfide.

8. The cyclic process of converting sodium sulfid into sodium sulfite, which comprises treating a solution of the sodium sulfid with sodium bicarbonate, removing from the solution hydrogen sulfid formed therein by agitating the treated solution and maintaining it at a temperature above 60° C., cooling the solution to a temperature below 60° C. after hydrogen sulfide has been removed therefrom, treating the resulting cooled solution with sulfur dioxide to form sodium sulfite and sodium bicarbonate, and returning the sodium bicarbonate for treating further amounts of sodium sulfid in the further carrying out of the process.

9. The cyclic process of treating solutions containing sodium carbonate and sodium sulfid, which comprises adding sodium bicarbonate to such a solution, agitating the solution at a temperature in excess of 60° C. to form and remove hydrogen sulfid from the solution and to give a sodium carbonate solution containing the original sodium carbonate and that formed by the reaction between the sodium sulfid and sodium bicarbonate, cooling the sodium carbonate solution and maintaining it below 60° C. while treating such solution with sulfur dioxide to form sodium sulfite and sodium bicarbonate, and returning the sodium bicarbonate for treating further amounts of a solution containing sodium carbonate and sodium sulfid.

10. The process of producing sodium sulfite

from sodium sulfid which comprises (a) treating the sodium sulfide in alkaline solution with solid sodium bicarbonate in amount sufficient to decompose the sodium sulfid thereof, thereby forming hydrogen sulfid and sodium carbonate; (b) heating the solution to remove hydrogen sulfid from the solution; (c) sulfiting sodium carbonate, resulting from step (a) in the presence of water, by means of available sulfur dioxide while the water is maintained at a temperature below 60 deg. C., thereby producing sodium sulfite in solution and also producing sodium bicarbonate; (d) separating solid sodium bicarbonate from the solution referred to in step (c); and (e) treating sodium sulfid in step (a) with sodium bicarbonate produced in step (c).

11. The process of treating residual liquor resulting from a digesting treatment of raw cellulosic-fibre-bearing material with a liquor that contains normal sodium sulfite and sodium carbonate, which comprises the following steps: (a) removing water from the residual liquor; (b) furnacing resulting carbonaceous matter and sodium-sulfur compounds under reducing conditions to produce sodium carbonate and sodium sulfid; (c) preparing an alkaline solution containing sodium carbonate and sodium sulfid thereby produced; (d) treating the alkaline solution with available carbon dioxide in amount at least as large as that which is chemically equivalent to the sodium sulfid therein, thereby converting sodium sulfid thereof into a carbonate of sodium and producing hydrogen sulfid; (e) removing hydrogen sulfid from the solution; (f) treating the solution while it is maintained at a temperature below 60 deg. C. with available sulfur dioxide, thereby obtaining sodium sulfite and sodium bicarbonate in the solution; and (g) digesting raw cellulosic-fibre-bearing material by means of the solution resulting from step (f).

12. The process of treating residual liquor resulting from a digesting treatment of raw cellulosic-fibre-bearing material with a liquor that contains a sulfite of sodium, which comprises the following steps: (a) removing water from the residual liquor; (b) furnacing resulting carbonaceous matter and sodium-sulfur compounds derived therefrom under reducing conditions to produce sodium carbonate and sodium sulfid; (c) preparing an alkaline solution containing sodium carbonate and sodium sulfid thereby produced; (d) treating the alkaline solution with solid sodium bicarbonate, produced by step (f), in amount sufficient to convert sodium sulfid thereof into a carbonate of sodium and form hydrogen sulfid; (e) removing hydrogen sulfid from the solution and burning the hydrogen sulfid to form gaseous sulfur dioxide; (f) maintaining the solution, resulting from steps (d) and (e), at a temperature below 60 deg. C. and sulfiting it with gases that carry sulfur dioxide so as to obtain sodium sulfite and sodium bicarbonate in the solution and also obtain some solid sodium bicarbonate; (g) separating such solid sodium bicarbonate from sodium sulfite and sodium bicarbonate contained in the solution; (h) treating such separated solid sodium bicarbonate with liquor as per step (d); and (i) sulfiting the solution separated by step (g) with available sulfur dioxide so as to convert a carbonate of sodium thereof into a sulfite of sodium for use in the further digestion of raw cellulosic-fibre-bearing material.

13. The further improvement in the process of claim 12, characterized by the use of sulfur di-

oxide formed by step (e) for sulfiting carbonate of sodium as per step (f).

14. The further improvement in the process of claim 12, characterized by the use of sulfur dioxide formed by step (e) for sulfiting carbonate of sodium as per step (i).

15. The further improvement in the process of claim 12, characterized by the step of introducing the residual liquor in finely divided condition into hot furnace gases produced by step (b) and subsequently introducing sodium-sulfur compounds thereof into a furnace for the carrying out of step (b).

16. The further improvement in the process of claim 12, characterized by the step of recovering sulfur dioxide from gases produced by step (b) and forming a sulfite of sodium that contains such recovered sulfur dioxide, and employing such sulfite of sodium in a cooking liquor for the digesting treatment therein referred to.

17. The further improvement in the process of claim 12, characterized by the step of passing relatively hot liquor resulting from step (e) countercurrent to a relatively cool liquor that contains a sulfite of sodium in order to cool the former and to heat the latter by means of a heat exchanger.

18. The cyclic process of treating residual liquor resulting from a digesting treatment of raw cellulosic-fibre-bearing material with a cooking liquor that contains a sulfite of sodium, which comprises the following steps: (a) evaporating water contained in the residual liquor; (b) furnacing resulting carbonaceous matter and sodium-sulfur compounds derived therefrom under reducing conditions to produce sodium carbonate and sodium sulfid and burning combustible matter also derived therefrom to produce furnace gases that contain sulfur dioxide; (c) preparing an alkaline solution containing sodium carbonate and sodium sulfid thereby produced; (d) treating the alkaline solution with available carbon dioxide to convert sodium sulfid thereof into carbonate of sodium and produce hydrogen sulfid; (e) removing hydrogen sulfid from the solution; (f) treating furnace gases mentioned in step (b) by means of liquor that contains a carbonate of sodium to recover sulfur dioxide therefrom and form a sulfite of sodium; (g) including the recovered sulfur dioxide in a cooking liquor that contains a sulfite of sodium and digesting raw cellulosic-fibre-bearing material therewith, thereby forming residual liquor; and repeating the process.

19. The further improvement in the process of claim 18, characterized by the utilization in step (f) of some carbonate of sodium in the solution resulting from the treatments set forth in steps (d) and (e).

20. In the process defined in claim 18, the further improvement which includes the following steps: (1) spraying the residual liquor into hot furnace gases formed by step (b), thereby evaporating water and recovering some sodium-sulfur compounds from the gases; (2) clarifying the sodium carbonate containing solution between steps (c) and (d); (3) burning the hydrogen sulfid removed by step (e) to form gaseous sulfur dioxide; (4) introducing sulfur dioxide thereby produced into a clarified sodium carbonate containing liquor subsequent to step (d) and step (e) to convert some of the sodium carbonate into sodium bicarbonate and some of it into sodium sulfite; (5) cooling the solution and separating solid sodium bicarbonate therefrom; and (6) using

such separated solid sodium bicarbonate to decompose sodium sulfid as per step (d).

21. In the art of treating residual liquor, resulting from a digesting treatment of raw cellulosic-fibre-bearing material with aqueous cooking liquor that contains a sulfite of sodium, in which art the water is evaporated and combustible organic matter thereof is burned to produce heat and sulfur and soda thereof are recovered and most of such recovered sulfur is used in forming a sulfite of sodium which is used in a subsequent similar digesting treatment, the improvement which comprises the following steps: (a) passing such residual liquor through hot furnace gases produced in step (b), thereby evaporating water, cooling the gases, and recovering a portion only of the oxy-sulfur constituents carried by the gases; (b) introducing into a furnace organic matter and sodium-oxy-sulfur compounds that were contained in such residual liquor, burning such combustible organic matter to produce heat, recovering soda and sulfur as sodium carbonate and sodium sulfid, and producing hot furnace gases that carry oxy-sulfur constituents including sulfur dioxide; (c) preparing an alkaline so-

lution that contains such recovered sodium carbonate and sodium sulfid; (d) treating such alkaline solution with solid sodium bicarbonate, produced in step (g) and separated in step (h), in amount sufficient to convert sodium sulfid thereof into carbonate of sodium and form hydrogen sulfid; (e) removing hydrogen sulfid from the solution; (f) burning such hydrogen sulfid to gaseous sulfur dioxide; (g) sulfiting the solution, resulting from steps (d) and (e), while maintaining it at a temperature below 60 deg. C., so as to produce sodium sulfite and sodium bicarbonate in the solution; (h) separating solid sodium bicarbonate from such dissolved sodium sulfite; (i) recovering sulfur dioxide produced by step (f) and also sulfur dioxide carried by the furnace gases after step (a) has been carried out and combining such recovered sulfur dioxide with carbonate of sodium contained in liquor resulting from steps (d) and (e); and (j) employing such recovered sulfur dioxide in the form of a sulfite of sodium in cooking liquor for a digesting treatment of raw cellulosic-fibre-bearing material.

LINN BRADLEY.

EDWARD P. McKEEFE.

### CERTIFICATE OF CORRECTION.

Patent No. 1,983,789.

December 11, 1934.

LINN BRADLEY, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, second column, line 45, for "cycle" read cyclic; page 4, first column, line 35, and second column, line 5, for "sulfite" read sulfide; page 11, first column, line 46, for "good" read wood; page 13, second column, line 71, for "corbonate" read carbonate; page 16, first column, line 38, claim 2, for "of" read containing; and page 17, first column, line 20, claim 11, for the syllable "car-" read bicar-; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 19th day of March, A. D. 1935.

(Seal)

Leslie Frazer  
Acting Commissioner of Patents.

such separated solid sodium bicarbonate to decompose sodium sulfid as per step (d).

21. In the art of treating residual liquor, resulting from a digesting treatment of raw cellulosic-fibre-bearing material with aqueous cooking liquor that contains a sulfite of sodium, in which art the water is evaporated and combustible organic matter thereof is burned to produce heat and sulfur and soda thereof are recovered and most of such recovered sulfur is used in forming a sulfite of sodium which is used in a subsequent similar digesting treatment, the improvement which comprises the following steps: (a) passing such residual liquor through hot furnace gases produced in step (b), thereby evaporating water, cooling the gases, and recovering a portion only of the oxy-sulfur constituents carried by the gases; (b) introducing into a furnace organic matter and sodium-oxy-sulfur compounds that were contained in such residual liquor, burning such combustible organic matter to produce heat, recovering soda and sulfur as sodium carbonate and sodium sulfid, and producing hot furnace gases that carry oxy-sulfur constituents including sulfur dioxide; (c) preparing an alkaline so-

lution that contains such recovered sodium carbonate and sodium sulfid; (d) treating such alkaline solution with solid sodium bicarbonate, produced in step (g) and separated in step (h), in amount sufficient to convert sodium sulfid thereof into carbonate of sodium and form hydrogen sulfid; (e) removing hydrogen sulfid from the solution; (f) burning such hydrogen sulfid to gaseous sulfur dioxide; (g) sulfiting the solution, resulting from steps (d) and (e), while maintaining it at a temperature below 60 deg. C., so as to produce sodium sulfite and sodium bicarbonate in the solution; (h) separating solid sodium bicarbonate from such dissolved sodium sulfite; (i) recovering sulfur dioxide produced by step (f) and also sulfur dioxide carried by the furnace gases after step (a) has been carried out and combining such recovered sulfur dioxide with carbonate of sodium contained in liquor resulting from steps (d) and (e); and (j) employing such recovered sulfur dioxide in the form of a sulfite of sodium in cooking liquor for a digesting treatment of raw cellulosic-fibre-bearing material.

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