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PRODUCTION OF PULP, ETC.

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This invention relates to improvements in the production of pulp and paper from wood, and in the treatment of the residual liquors from such pulp-making operation, and the production of cooking liquor for use therein. The invention includes improvements in the treatment of residual liquors, in the production of cooking liquor, in the pulp-making process, and in the cyclic or regenerative process in which the residual liquors from the process are treated for the production of further amounts of cooking liquor. More particularly the invention relates to improvements in the production of pulp from wood with the use of a mono-sulfite cooking liquor, such as a sodium mono-sulfite cooking liquor, used in sufficient amount to prevent the cooking liquor from becoming acid to litmus during the cooking operation, so that the residual liquor is alkaline to litmus, and in the treatment of residual liquors from such process and the production of cooking liquors therefor, as well as a cyclic process in which the cooking liquors are regenerated from the residual liquors.

This application is a continuation in part of our prior applications, Serial No. 481,147, filed June 28, 1921, Serial No. 534,768, filed February 7, 1922, and Serial No. 711,857, filed May 8, 1924.

The pulp-making processes heretofore and still commonly employed, are the so-called soda process, in which the cooking liquor is made up essentially of caustic soda; the so-called sulfate process, in which the cooking liquor is made up essentially of caustic soda and sodium sulfid; and the so-called sulfite process, in which the cooking liquor is made up of an acid solution of a sulfite, usually calcium bi-sulfite. The sulfite cooking liquor is strongly acid, while the soda and sulfate cooking liquors are strongly alkaline to phenolphthalein. In the sulfite process, in which a large excess of free sulfurous acid or sulfur dioxide is used, it is usual to withdraw or relieve gases from the digester, and recovery systems are used to recover the sulfur dioxide thus driven off or relieved, in order to avoid loss and recover it for further use in the process. In the soda and sulfate processes, the cooking liquors are free from an acid character.

The improved process of the present invention, as distinguished from the above, is one in which the cooking liquor is free from any large amount of caustic alkali, although moderate and varying amounts of sodium carbonate, caustic alkali, sodium sulfid, etc., may be present. The present process is one in which sodium monosulfite is used as the principal constituent of the cooking liquor, with small and varying amounts of other sodium salts, such as those which may be incidental to the production of the sodium sulfite cooking liquor, or such as may be incidental to the regeneration of the cooking liquor from the residual liquor. Among the other sodium compounds that may be present, are sodium carbonate, sodium sulfid, sodium thiosulfate, caustic soda, sodium sulfate, et cetera.

When the sodium monosulfite cooking liquor is regenerated from the residual liquor from such cooking operation by concentrating and carbonizing or by smelting the carbonized product or by other further treatment and then leaching or dissolving the soluble sodium salts from the resulting product, the solution will contain sodium carbonate as the main, or one of the main, sodium salts, depending on how the carbonizing or smelting operation is carried out. If the carbonizing is carried out, for example, in a rotary furnace, such as is commonly used for making black ash in a soda mill, the carbonizing can be regulated so that a considerable amount of sodium monosulfite is directly obtained in the leached liquor, but considerable amounts of sodium carbonate are also obtained. If the calcining or smelting is carried out under reducing conditions, the resulting solution or liquor will contain a large amount of sodium carbonate and may contain varying amounts of sodium sulfid, sodium sulfite, sodium thiosulfate, sodium sulfate, et cetera. In order to regenerate a suitable monosulfite cooking liquor from such a leached liquor or solution, the carbonate advantageously is converted into sulfite in whole, or for the most part, although some of it may be converted into other compounds, or may remain as a corbonate. If such unsulphited solution is directly sulfited with sulfur dioxide, part or all of the sodium sulfid present may be converted into sodium thiosulfate, depending on conditions, while some or all of the sodium carbonate may be converted into sodium sulfite, but varying amounts of a carbonate of sodium may remain in the sulfited liquor, if the sulfiting is stopped before complete sulfiting, or if the acid sulfited liquor is neutralized by adding sodium carbonate. Such regenerated cooking liquors may, therefore, contain a carbonate of sodium.

The presence of carbonate in substantial amount, in such cooking liquors, has an effect which seems to be peculiar in that the carbon dioxide is set free during the digestion or cooking operation, and this interferes with the carrying out of the operation of the digestion, unless the interference is overcome.

According to the present invention, the cooking operation is carried out with a monosulfite cooking liquor, particularly sodium monosulfite cooking liquor, containing sufficient active chemicals to cook wood and produce satisfactory pulp, and the cooking operation is promoted by withdrawing gases from the digester during the cooking operation. This withdrawal or relief of gases from the digester promotes circulation during the progress of the digestion, avoids excessive false pressures, enables volatile constituents, such as turpentine, etc. to be recovered from resinous woods, and permits the use of regenerated cooking liquors to particular advantage.

The present invention also includes improvements in the treatment of the cooking liquor before it is charged into the digester, as well as the operation of the digester by releasing gas therefrom preliminary to or during the digestion.

According to one embodiment of the invention, the regenerated cooking liquor, containing mainly sodium sulfite, but also containing a carbonate of sodium, and may also contain varying amounts of other sodium compounds, such as sodium sulfid, sodium thiosulfate, caustic soda, sodium sulfate, etc., is subjected to a preheating or boiling operation before it is charged into the digester, and carbon dioxide is in this way driven off so that the liquor as charged into the digester is free, or nearly so, from uncombined or loosely combined carbon dioxide.

According to another embodiment of the invention, the regenerated cooking liquor, containing a carbonate of sodium, is treated with calcium sulfite, with resulting precipitation of calcium carbonate, and formation of a corresponding amount of sodium sulfite in the solution, in addition to the amount of sodium sulfite previously present. Instead of using calcium sulfite, a mixture of calcium sulfite and lime can be used, particularly where a small amount of caustic soda is desired in the cooking liquor. In such case, any sodium sulfid present in the regenerated liquor will remain in the cooking liquor. So also, other compounds, such as magnesium sulfite, etc. can be used, which will form a carbonate precipitate and thus remove carbonate radical from the solution, and which will convert an equivalent amount of the sodium carbonate into sodium sulfite or other unobjectionable or desirable sodium compounds for use in the process. This preliminary treatment may be carried to the point of substantially complete removal of carbonate from the cooking liquor, or a partial removal can be effected, and further removal can be effected by relief from the digester during the preliminary heating or during the main cooking operation or both.

Instead of preheating the cooking liquor, or treating it otherwise, before it is charged into the digester, it may be heated in the digester before the main cooking operation is begun, and part of the carbon dioxide driven off from the digester during the heating-up period, or during the preliminary part of the digestion period.

The cooking operation can be carried out in accordance with the procedure more fully described in our prior application, Serial No. 481,147, of which the present application is a continuation in part. The wood chips can be cooked, for example, with upwards of thirty per cent of monosulfite on the air dry weight of the wood, (i. e., wood containing ten per cent of water) in the case of deciduous and some coniferous woods, and upwards of thirty-five per cent for resinous woods, together with varying amounts of other sodium salts. With poplar, birch and other deciduous woods, the amount of sodium monosulfite may be e. g. from 30 to 40 per cent, and for coniferous woods, such as pine or spruce, about 35 to 45 per cent on the air dry weight of the wood. Digesters of iron or steel are well adapted for use in the process of the present invention. The digester can be heated, for example, by direct steam at a steam pressure varying from about 110 to 140 pounds and for a suitable period of time, e. g., from ten to three hours.

During the carrying out of the digestion, when resinous woods are treated, the turpentine can be removed from the digester by "bleeding" the digester, that is, by permitting part of the gases to escape from the digester at successive time intervals; and this bleeding operation will also permit the escape and relief from the digester of carbon dioxide gas. Also, in order to promote circulation during the progress of the digestion, it may be advantageous to relieve the internal pressure of the digester for a short period; and this relief of the internal pressure may be accompanied by the removal of carbon dioxide. This relief can be accomplished by opening a valve in a pipe line leading from the top of the digester to the blow pit. When a suitable reduction in pressure has been obtained, the valve is again closed and circulation of the cooking liquor within the digester continues. The digestion is continued until the wood has been sufficiently cooked, whereupon the charge can be blown from the digester to the blow pit, and the residual liquor then drawn off from the pulp, and treated for the regeneration of cooking liquors therefrom.

The process is applicable to the treatment of both deciduous and coniferous woods, including not only the common pulp woods, such as poplar and spruce, but including more particularly the woods which are not commonly considered pulp wood, or which have not been considered available for the production of high grade pulp. The invention is also applicable to other deciduous woods, including heavy hard wood, such as birch, beech and maple, or oak, et cetera. It is also applicable to coniferous woods, both those which are highly resinous, such as pines, as well as coniferous woods which are lower in resin content, or which may be free therefrom. The process results in the production of an increased yield of the various pulps, as compared with present day processes.

The residual liquor from the cooking operation may contain sodium sulfite in appreciable amount, particularly where a substantial excess of sodium sulfite is used during the cooking operation. In addition, the liquor frequently contains sodium compounds of organic acids, such as sodium acetate, et cetera, or sodium "resinate".

The residual liquor is advantageously treated by concentrating in multiple effect evaporators and by feeding the concentrating liquor into a carbonizing or smelting furnace, such as a rotary calcining or carbonizing or smelting furnace, or carbonizing and smelting furnaces such as are commonly used in the so-called sulfate process. The concentrated liquor may, for example, be fed into a rotary calcining furnace and there carbonized under regulated conditions to avoid smelting to any considerable extent, so that there will be little, if any, sulfid present in the calcined product, and so that sodium sulfite in appreciable amount may still be contained in the carbonized product. When the carbonized product is leached with water, or with a suitable solution, it will

dissolve the soluble sodium compounds, of which sodium carbonate will be one of the prominent, if not the main constituent. When the carbonized product is subjected to a smelting operation and the melt dissolved, the soluble compounds will be made up largely of sodium carbonate, and sodium sulfid, together with varying amounts of sodium sulfate, and smaller amounts of sodium thiosulphate, sodium sulphite, etc.

The further treatment of the leach liquor or of the solution of the melt will depend upon the character of its composition and the nature of the cooking liquor desired.

Where the solution contains considerable amounts of sodium sulfite, and little, if any, sodium sulfid, it can be directly sufited by treatment with sulfur dioxide to convert most of the carbonates into sodium sulfite. If small amounts of sodium sulfid are present, they will be converted to a greater or less extent into sodium thiosulfate by reaction with the sulfur dioxide, although some of the sodium sulfid may be decomposed and hydrogen sulfide driven off, depending on the conditions. The sulphiting of the solution is terminated before all of the carbonate has been acted upon by sulfur dioxide, or, if continued so as to produce some sodium bisulphite, sodium carbonate may be added thereto. In either case, however, there will be some carbonate left in the sulfited liquor.

In case a melt is obtained, or in case the calcining is carried out under reducing conditions, there will be more or less sodium sulfid present in the resulting solution, together with varying amounts of other compounds, mainly sodium carbonate. If the amount of sulfid is large, it will not ordinar. be advisable to subject the liquor directly to s .fiting with sulphur dioxide, without suitable precautions, because of the large amount of sodium thiosulfate which would be formed, although sodium thiosulfate may be desirable to a limited extent in the cooking operation, as described more fully in our prior application, Serial No. 704,176, filed April 4, 1924. The amount of thiosulfate formed can be limited and regulated, for example, by first treating the solution with carbon dioxide, to decompose part or all of the sodium sulfid, and driving off the hydrogen sulfid, and by then sulfiting the resulting solution, after it has been partly or substantially completely freed from sulfid. By regulating the carbonating and sulfiting operations, it is possible to produce a regenerated solution made up mainly of sodium sulfite, with varying and regulated amounts of sodium thiosulfate, either with or without small amounts of other sodium compounds, such as sodium carbonate, sodium sulfate, et cetera.

Instead of sulfiting the leached liquor or solution of the melt, particularly when sodium sulfid is present therein in appreciable or considerable amounts, advantage may be taken of this sodium sulfid in the formation of cooking liquor, so that the cooking liquor will contain sodium sulfid, as well as sodium sulfite, and either with or without other compounds, such as sodium thiosulfate, caustic soda, et cetera. By subjecting the solution, containing sodium carbonate and sodium sulfid, to treatment with calcium sulfite, or a mixture of calcium sulfite and calcium carbonate, the calcium sulfite will react with the sodium carbonate to form calcium carbonate, which is insoluble, and which can be separated as a precipitate, and sodium sulfite, which remains in solution. This method of sulfiting the solution enables substantially all of the carbonate to be removed therefrom, while leaving the sodium sulfid in the solution. In this way a cooking liquor made up mainly of sodium sulfite, with varying amounts of sodium sulfid, can be produced. By adding sodium sulfate, or sodium bisulfate or otherwise increasing the sulphate content of the residual liquor before or during its concentration, or to the concentrated liquor before or during the carbonizing and smelting operations, an increased amount of sodium sulfid can be formed and utilized in making additional amounts of cooking liquor, in which sodium sulfite and sodium sulfid are the main constituents.

By using, instead of calcium sulfite, a mixture of calcium sulfite and calcium hydroxide, some of the sodium carbonate can be converted into caustic soda, giving a resulting liquor made up mainly of sodium sulfite, together with a regulated amount of caustic soda, or with both caustic soda and sodium sulfid present in regulated amounts and either with or without the presence of sodium thiosulfate, either obtained by leaching the calcined or smelted product, or by a regulated sulfiting of a solution containing sodium sulfid.

Where the carbonate is removed with substantial completeness from the liquor by treatment with calcium sulfite, or by other treatment, it will not, of course, be necessary to subject the resulting liquor to further special treatment or remove carbonate.

Where, however, the regenerative process gives a liquor which contains carbonate, this liquor can be subsequently treated for the removal of carbonate radicle either before or during its use as a cooking liquor.

One method of carrying out this further treatment is to preheat the liquor and agitate it to promote the driving off of carbon dioxide therefrom. It may be heated, for example, by the steam and gases releieved from the digester. The preheating of the liquor not only serves to remove a greater or less amount of the carbon dioxide therefrom, but also promotes the cooking operation by shortening the time required to heat the digester charge to the cooking temperature.

Fo a digester of about eight feet in diameter and 25 feet high, about 4000 gallons or more of a suitable cooking liquor may be used for cooking a digester full of poplar chips, the liquor containing an amount of mono-sodium sulfite equal to about 35 to 40 per cent of the air dried weight of the wood, together with such other sodium salts as may be present along with the sodium sulfite in the regenerated liquor or in liquor made, for example, by sulfiting a solution of sodium carbonate or soda ash. The chips may be charged into the digester while it is still hot from the previous cooking operation, or the liquor and chips can be run in together into the digester simultaneously. When sufficient chips and liquor have been run in to permit the establishment of the circulation of liquor, steam can be turned on both below the main body of chips and so as to direct the liquor upward through the circulating pipe, so the circulation of the liquor is established and maintained while the chips are being run into the digester. When the digester has been filled and closed, it is then brought up to temperature and pressure as rapidly as practical, using direct steam. The temperature and pressure are thereafter maintained nearly constant, for example, at a pressure of about 120 pounds per square inch, until the cooking operation is finished, except for

the relief of the internal pressure of the digester for short periods of time, which can be accomplished by opening a valve in a pipe line leading from the top of the digester to the blow pit. When a suitable reduction in pressure has been obtained, the valve is again closed and circulation of the cooking liquor within the digester continued, steam being turned in partly for this purpose. The time required to bring the digester to the desired temperature and pressure may be, for example, about one or two hours, and the cooking operation for poplar wood may require from four to six hours at pressure for its completion, although a longer or shorter time may be used. So, also, the amount of sodium sulfite may be somewhat increased or decreased from that above indicated. So, also, different saturated steam pressures may be used, e. g., of about 110 to about 140 pounds to the square inch, with a corresponding temperature; that is, the saturated steam pressure will depend upon the temperature of the steam or water within the digester.

When the cooking operation has been finished, the digester may be blown in the usual manner. The pulp and residual liquor can then be run into vats or tanks and the residual liquor separated more or less from the pulp, the pulp then washed in the usual way, and the washed pulp then subjected to further treatment. The residual liquors can be separately treated for the production of further amounts of cooking liquor therefrom.

As an example of the cooking of wood with a cooking liquor containing a small amount of caustic soda during a part of the cooking operation, and which may be regenerated from the residual liquor, highly resinous Georgia pine, which has been air-seasoned, may be taken as an example. Such wood after chipping may be cooked in a digester for a suitable period, (for example, for about four hours or more) at a temperature corresponding to a saturated steam pressure of about 120 pounds per square inch, using a cooking liquor containing an amount of normal sodium sulfite equal to about 35 to 40 per cent of the weight of the wood (figures on an air-dried basis); then removing the larger portion of the cooking liquor from the digester, and introducing a further amount of cooking liquor, containing a few per cent of caustic soda (e. g. 3 to 10 per cent) in addition to the sodium sulfite (e. g. 20 to 25 per cent), and cooking the chips at a temperature corresponding to a saturated steam pressure of about 120 pounds per square inch for an additional period of about four hours. In addition to the sodium sulfite, the cooking liquor may contain small amounts of other sodium salts produced during the regenerating operation. By proceeding in this way, the highly resinous pine wood can be thoroughly cooked, and the cooked wood readily and easily pulped.

During the carrying out of the digestion with such resinous wood, the turpentine &c. can be removed from the digester by "bleeding" the digester, that is, by permitting part of the gases to escape from the digester at successive time intervals; and along with the bleeding of the turpentine, there will also escape more or less of the carbon dioxide, in case the cooking liquor contains a substantial amount of carbonate when charged into the digester at the beginning of the cooking operation.

With resinous woods, we found it particularly advantageous to charge the chips into the digester, and to charge the digester with the sodium sulfite cooking liquor sufficient for the cooking of the digester charge, and then to subject the digester charge to a preliminary heating operation at a temperature below the critical temperature of reaction for a sufficient time to insure that the chips are thoroughly treated with the liquor and with the sodium sulfite thereof, before the digester charge is later heated to the active cooking temperature. This preliminary heating will serve to drive off to a greater or less extent any carbon dioxide contained in the liquor as carbonate and particularly as bicarbonate. After the proper impregnation has been accomplished in the digester, the temperature of the digester charge may then be raised higher and the digestion then carried to completion. One advantageous method of charging the digester and of effecting the preliminary impregnation and heating, is to partially charge the digester with the wood chips and then add the cooking liquor and then heat the cooking liquor gradually to a temperature of above 100° C. and charging additional wood chips during the gradual heating period referred to.

During the cooking operation, the volatile constituents driven off from the resinous wood, for example, turpentine, etc., may be removed from the digester by bleeding, that is, by permitting part of the gases to escape from the digester, including carbon dioxide gas when present therein. These may be cooled and liquids recovered for subsequent treatment or use. This method of carrying out the cooking operation with preliminary impregnation of the charge at a temperature below the critical temperature, is more fully set forth in our prior application, Serial No. 711,857, of which the present application is a continuation in part. As pointed out in said application, it is advantageous for resinous woods to use temperatures around 175 or higher, for example, around 180 to 190 degrees C., and it is one advantage of the process that it permits the use of such high temperatures with resinous woods, particularly where the wood chips are subjected to a thorough preliminary impregnation in the manner above indicated. This preliminary treatment also has the advantage above mentioned of driving off carbon dioxide when present in the digester, introduced as carbonate or bicarbonate in the cooking liquors; while the relieving of turpentine along with other gases, provides further opportunity for the escape of carbon dioxide from the digester.

The cooking liquor in this process, while it is made up mainly of sodium sulfite, may contain other sodium compounds of the character hereinbefore mentioned; particularly a carbonate of sodium, sodium thiosulfate or other oxy-sulphur compounds or caustic soda, sodium sulfid, sodium sulfate, etc. These other sodium salts may be present in moderate amounts, where the cooking liquor is regenerated from the residual liquors of the process.

Instead of using the regenerated cooking liquor, the cooking liquor may be directly produced from sodium carbonate, for example, by sulfiting it with sulfur dioxide. When the sulfiting is continued until the solution contains a small amount of free sulfur dioxide, i. e. as sodium bisulfite, a predetermined amount of sodium carbonate can be added to bring the liquor back until it is alkaline to phenolphthalein when cold after boiling. Such a liquor consists almost entirely of a solution of normal sodium sulfite, free from sodium

thiosulfate, etc., but containing moderate and varying amounts of carbonate.

In the cooking of resinous woods with such a cooking liquor, the wood chips, for example, spruce chips, can be charged into the digester, together with the cooking liquor, and the digester charge then heated gradually by the introduction of steam, such that, for example, the steam pressure increases to about 80 pounds after two and one-half hours, and to 110 after three and one-quarter hours, and 140 pounds in three and one-half hours. During this preliminary period taken in bringing the digester to pressure, the relief valve can be occasionally opened for short intervals to permit of removing gas, steam, etc., and for promoting the circulation of the cooking liquor. When carbon dioxide is present in the digester, it will be to a greater or less extent removed during these relief periods. Relief may be effected, for example, by opening the relief valve until the pressure is reduced about 8 or 10 pounds, and then closing the valve. After the digester has reached the desired pressure, e. g. 140 pounds pressure in the upper portion of the digester, this pressure can be maintained for a further period of time to complete the cooking operation, with opening of the relief valve for about five minutes at a time at each half hour period during the further cooking operation. This opening and closing of the relief valve facilitates circulation of the cooking liquor, as well as escape of carbon dioxide and other gases from the digester. The cooking of resinous wood in accordance with this procedure is more fully described in our said prior application, Ser. No. 711,857.

Instead of using fresh cooking liquor, freshly made from pure sodium carbonate by sulfiting, regenerated cooking liquors containing sodium sulfite as the main constituent, but also containing other sodium salts in varying amounts, such as sodium sulfid, sodium thiosulfate, sodium sulfate, caustic soda, etc. can be used.

For example, poplar or aspen, after barking and chipping, can be charged into the digester to the extent of, for example, eight cords of wood measured before chipping, together with 1000 cubic feet of hot cooking liquor, containing 6500 to 8000 pounds of sodium sulfite, about 500 to 2000 pounds of sodium carbonate (partly as bicarbonate) and 500–2000 pounds or so of sodium thiosulfate, together with a moderate amount of sodium sulfate and sodium sulfide. Such a cooking liquor can be produced, for example, from the residual liquor of the process, by evaporating and calcining, with or without smelting, to give a product containing carbonate and sulfid and by sulfiting the solution thereof to convert the sodium sulfid for the most part into sodium thiosulfate, as well as to convert sodium carbonate for the most part into sodium sulfite, leaving, however, varying amounts of sodium carbonate unsulfited, and present partly as sodium bicarbonate. By preheating the liquor at a sufficiently high temperature and for a sufficient period of time, the bicarbonate present can be largely converted into sodium carbonate before charging the liquor into the digester, in which case there will be a correspondingly less amount of carbon dioxide to be removed from the digester. Where, however, the cooking liquor is charged into the digester without such treatment, the digester charge can be gradually heated, with circulation of the liquor in the digester, for example, by means of a pump, and with introduction of steam into the circulating line, e. g., until a pressure of around 60 to 80 pounds gauge is obtained. By then stopping the pump circulation and continuing to introduce steam into the digester through a steam ring, and by relieving gases from the top of the digester, the carbon dioxide can be progressively removed. The relieving of gases from the digester not only removes carbon dioxide, but also materially helps the digester circulation. The gases relieved can be employed to preheat cooking liquor of a similar type for subsequent digester charges, if desired. Where large amounts of carbonate are present in the cooking liquor, a correspondingly increased amount of relief of gases is required. Preheating of such a cooking liquor by the relief from the digester results in heat economy and shortening of the subsequent digestion because of the shorter time required for bringing the digester to the necessary pressure. Where, for example, the cooking liquor is preheated to about 80 or 100° C. when charged into the digester, a gauge pressure of around 130 to 135 pounds on the digester top can be obtained in a period of around one hour or so, and the temperature of the cooking liquor will be above 170° C. The temperature may be further increased by continuing to introduce steam of a higher temperature. This is facilitated by relieving the digester and removing gas, steam pressure from 150 to 175 pounds gauge being suitable for this purpose.

With coniferous woods an increased amount of sodium sulfite is generally required as compared to poplar in the cooking liquor, and, where the cooking liquor contains sodium carbonate, a correspondingly increasing amount of sodium carbonate is generally present in the digester charge of liquor. A charge of around 8 cords of tamarack chips, for example, cooked with 1000 cubic feet of a cooking liquor containing from 8700 to 10,000 pounds of sodium sulfite, i. e. Na_2SO_3, and with the other sodium compounds in the proportions above indicated, can be heated slowly during a period of about three hours or so, to bring the charge to a pressure of around 130 to 135 pounds gauge, with relief during this bringing-up period, to promote the escape of carbon dioxide, etc., care being taken to maintain copious circulation throughout the charge. The carbon dioxide, unless removed, hinders the uniform circulation of the liquor, and may otherwise be objectionable. The charge, after being brought to temperature, may be cooked by the introduction of direct steam (super-heated, if desired) at around 150 to 175 pounds steam gauge on the steam line.

At the end of the cooking operation, the digester charge is blown to the blow-pit and the residual liquor separated and treated for the regeneration of cooking liquors therefrom. This regeneration, as above outlined, may advantageously be effected by concentrating the liquor in multiple effect evaporators and leading the concentrated liquor into rotary calcining furnaces to carbonize the organic matter and convert the sodium compounds present in the residual liquor into a form such that they can be leached from the product in the form of a solution suitable for use for the preparation of cooking liquor therefrom. The concentration in multiple effect evaporators is advantageously carried to a high concentration of about 35° Bé. at 90° to 100° C. The residual liquor may be treated by itself, or it may be admixed with residual liquor from a process in which other cooking liquors have been used,

for example, a cooking liquor containing a preponderating amount of caustic soda and a smaller amount of sodium sulfite, either with or without other sodium salts, such as sodium sulfid, as described in our prior applications, Serial Nos. 535,034, filed February 8, 1922, and Serial No. 713,257 filed May 14, 1924. A residual liquor resulting from the cooking of poplar, birch, etc., with a cooking liquor containing mainly caustic soda and sodium sulfite, or caustic soda, sodium sulfite and sodium sulfide, with or without varying amounts of sodium thiosulfate, etc., may be admixed with a residual liquor from the cooking of wood, with a cooking liquor containing mainly sodium sulfite, with or without other sodium compounds of the character hereinbefore mentioned, and the mixed residual liquor then evaporated to a concentration of about 35° Bé. at a temperature of from 90° to 100° C. The organic compounds in the concentrated residual liquor can then be decomposed and the resulting sodium compounds can be dissolved to give a liquor, containing mainly sodium carbonate, but with varying amounts of other sodium compounds such as sodium sulfid, sodium sulfite, sodium thiosulfate, and sodium sulfate. The liquor, after clarifying, if necessary, can be directly sulfited, or sulfited and partially causticized to a limited extent, to regenerate the cooking liquor. The sulfur dioxide for the sulfiting operation may be obtained from a sulfur burner in the usual manner, or from some other source, such as the relief gases of an acid sulfite cooking process. If the sulfiting operation is carried out cold with sulfur dioxide, a considerable amount of sodium thiosulfate will be formed where sodium sulfid is present in the liquor, although some hydrogen sulfide may be liberated and some elementary sulfur may be formed and carried off with the gases.

Instead of directly sulfiting the liquor, particularly where it contains sodium sulfid, it may be first treated with carbon dioxide or sodium bicarbonate to decompose the sodium sulfid and drive off hydrogen sulfid, preferably heating the solution during or after the carbonating, and then be sulfited to convert the carbonate into sulfite, as more fully described in our prior application, Serial No. 686,137, filed January 14, 1924. The unsulfited liquor can thus be run through a suitable carbonating tower where it is subjected to carbon dioxide gases with the removal of hydrogen sulfide and then through another suitable tower, where it is subjected to sulfur dioxide gases. In this way the sodium sulfid will be more or less converted into a carbonate of sodium before the sulfiting treatment.

When the liquor has been sulfited so that it contains only about one-half pound to two pounds of sodium carbonate per cubic foot, (most of which may be as sodium bicarbonate) it is ready for use as a cooking liquor; but by heating it high enough and by prolonged agitation, most of the sodium bicarbonate can be converted into sodium carbonate, thus reducing the amount of carbon dioxide to be removed after the digester cover has been placed. By circulating the digester content, i. e., of liquor, with the cover off, and by heating by direct steam to nearly the boiling point, appreciable amounts of carbon dioxide can be removed before the cover is fastened in place.

Where the sulfiting operation is continued until the liquor contains no sodium carbonate or bicarbonate, but an excess of sulfur dioxide, i. e., some sodium bisulfite, and then adding a moderate excess of sodium carbonate, it can be subjected to heating and prolonged agitation and circulation, until most of the dissolved and loosely combined carbon dioxide is driven out; the liquor now being alkaline to phenolphthalein due to the presence of sodium carbonate; or the sulfited liquor may be itself subjected to heating and agitation until most of the carbon dioxide is driven out, and then caustic soda added until the liquor is moderately alkaline to phenolphthalein. The amount of alkali to be added can be determined by analysis. In this way, by acidifying the solution when it is sulfited, then heating to drive out dissolved carbon dioxide, and then adding caustic soda to neutralize the excess acid and give a solution moderately alkaline to phenolphthalein (e. g. about .25 to .75 pound of caustic soda per cubic foot of liquor), the cooking liquor can be substantially freed from carbon dioxide before it is charged into the digester. The liquor at the time it is sulfited will ordinarily be much more concentrated than is desired for the cooking operation; but this strong liquor can be mixed with the necessary amount of water, or with some residual liquor from the process, to give a cooking liquor of proper composition, for example, a cooking liquor such that 1000 cubic feet more or less of the liquor, will be used for about 8 cords of poplar wood, and will contain about 6500 to 8000 pounds of sodium sulfite. Such a liquor for tamarack wood will contain, for example, from 8700 to 10,000 pounds of sodium sulfite, i. e. Na_2SO_3.

By using caustic soda for neutralizing the acidity, after the dissolved carbon dioxide has been substantially completely removed, the difficulties due to carbon dioxide during digestion, are eliminated, so that good circulation and more uniform cooking conditions can be readily obtained and the need for relief of gases is correspondingly reduced.

Another method of treating the liquor is to sulfite it until there is a small amount of sodium carbonate or bicarbonate left in the sulfited liquor, or even until all carbonate is converted into sulfite, etc., and then add enough calcium oxide or heavy milk of lime, so that the strong cooking liquor will contain approximately .25 pound to 1.0 pound, caustic soda per cubic foot, and from 8 to 10 pounds of sodium sulfite, (Na_2SO_3) per cubic foot. The carbonate present will be converted into calcium carbonate, which will be precipitated. Some calcium sulfite may be simultaneously precipitated, and these precipitates will assist in clarifying the solution by sedimentation or by filtration. The precipitates obtained, containing calcium carbonate or calcium sulfite and calcium carbonate together with calcium hydroxide, etc., can be washed and its contained cooking liquor recovered. The precipitates can then be treated with sulfur dioxide to convert calcium carbonate and calcium hydroxide into calcium sulfite, which can then be used for treating further amounts of liquor, to remove carbonate therefrom, and to supply additional amounts of sulfite radical to the liquor, by interaction of calcium sulfite and sodium carbonate to form sodium sulfite, which remains in solution, and calcium carbonate, which precipitates as an insoluble product.

Another method of treating the liquid, or solution containing the sodium carbonate, together with other salts, particularly sodium sulfid, is to carry out the sulfiting operation while the liquor is hot, e. g., at a temperature above 80° C., using sulfur dioxide or better, a sodium bisulfite solu-

tion. By sulfiting a solution of sodium carbonate or leached liquor at such elevated temperature, most of the carbon dioxide when free will be driven off, so that the sulfited liquor will contain little, if any, carbon dioxide, either as free carbon dioxide, or as sodium bicarbonate, if the liquor is sulfited until it is neutral to phenolphthalein after prolonged boiling and then cooling. It can be boiled and agitated to remove more carbon dioxide, if any objectionable amount is still left in the liquor. By causticizing the liquor to a limited extent with calcium hydroxide, after sulfiting until substantially all of the carbonates have been acted on by SO_2, any residual carbonate can be converted into caustic soda, or even sodium sulfite may be in part converted into caustic soda. When the liquor contains sodium sulfid, the sulfited liquor may contain more or less sodium thiosulfate. A cooking liquor may thus be obtained, in the manner above described, which contains about 10,000 pounds of sodium sulfite, about 600 pounds of sodium thiosulfate, and about 700 pounds of caustic soda in about 1000 cubic feet of cooking liquor with substantially no carbon dioxide either free or combined as sodium carbonate or bicarbonate.

During the digestion, when carbonate is present in the cooking liquor in small amounts, the liquor can be kept alkaline to phenolphthalein by the gradual introduction of caustic soda into the digester during the cooking period.

The caustic soda, which is so added during the cooking period, as well as caustic soda which may be desirable in the cooking liquor to a regulated extent, may be produced by causticizing a part of the leach liquor or solution obtained from the calcined product or from the melt, as herein described, in which case it may contain varying amounts of sodium sulfite or sodium sulfid, or other sodium salts, and will add such salts, as well as caustic soda, to the cooking liquor.

Where a considerable amount of carbonate is present in the cooking liquor, and there is a considerable amount of relief of gases to effect sufficiently complete removal of the carbon dioxide from the digester, a considerable amount of steam escapes, causing a high steam loss. The relief gases, however, can be utilized to pre-heat cooking liquor for a successive charge, so that its heat can be recovered to a greater or less extent. This preheating of cooking liquor, before charging the digester, assists in the removal of dissolved carbon dioxide, as well as carbon dioxide present as bicarbonate, thus reducing the amount of carbon dioxide which is charged into the digester; while the gases relieved from the digester can be recovered in a steam accumulator so that the heat which they contain can be taken advantage of.

We have further found that when a leached liquor, or solution containing sodium carbonate and some sodium sulfid is subjected to sulfiting while it is hot, e. g. above 80° C., and particularly if sodium bisulfite is added gradually to the boiling solution to effect the sulfiting, the sodium sulfid is, for the most part, decomposed and hydrogen sulfide driven off without any such large formation of sodium thiosulfate as takes place when the leached liquor or solution is sulfited with sulfur dioxide in the cold. The sulfiting hot also has the advantage above mentioned, of assisting in driving off dissolved and loosely combined carbon dioxide from the sulfited solution.

When the sulfited solution is treated with lime to remove the carbonate as calcium carbonate, more or less calcium sulfite may be simultaneously precipitated. The resulting precipitate, with adhering liquor, may advantageously be used for treating leached liquor which has not been sulfited, so that the calcium sulfite will react with sodium carbonate to form additional sodium sulfite and give a precipitate made up, mainly of calcium carbonate. If excess lime is present admixed with the first precipitate, it will have a causticizing effect upon the second solution, which will accordingly be both sulfited and causticized to the extent of the calcium sulfite and calcium hydroxide which the first precipitate contains. The second calcium carbonate precipitate can be sulfited with sulfur dioxide to form calcium sulfite, which can similarly be used upon a solution containing sodium carbonate, or sodium carbonate and sodium sulfid, etc., to convert sodium carbonate into sodium sulfite, with resulting precipitation of calcium carbonate.

It will thus be seen that the present invention includes improvements in the cooking operation for the production of chemical pulp from wood with a monosulfite cooking liquor, such as sodium monosulfite cooking liquor; that the invention also includes improvements in the treatment of the residual liquors from such process, and in the preparation of cooking liquors for such process. It will also be seen that the invention includes a cyclic process in which the cooking operation is carried out with a sodium monosulfite liquor, the residual liquor subjected to concentration and calcining, either with carbonizing or smelting, and the products extracted or leached or dissolved to give a solution containing sodium carbonate with varying amounts and proportions of other sodium compounds; and that the resulting solution is subjected to treatment such that the carbonate is converted for the most part into sulfite, and that the resulting sulfited liquor is further subjected, either preliminary to or during the further cooking operation, to remove therefrom the objectionable excess of carbon dioxide which may be contained in a dissolved or loosely combined form, or as sodium bicarbonate, or in some cases as sodium carbonate where the latter is present in considerable amounts.

It will further be seen that the invention provides different methods of treatment of the regenerated solution for the preparation therefrom of a cooking liquor and the elimination of any objectionable excess of carbon dioxide, as well as improvements in the treatment of the residual liquors and the production of cooking liquors. The preliminary treatment of the cooking liquors to remove any objectionable excess of carbon dioxide therefrom correspondingly relieves the digestion operation of the need for such removal. Where, however, there is an excess of carbon dioxide in free or combined form introduced into the cooking liquor, carbon dioxide may be removed during the preliminary cooking operation, or in part during such preliminary operation and in part during the main cooking operation, by relieving gases, including carbon dioxide, from the digester, along with other gases and vapors, such as turpentine in the case of resinous woods. The preliminary treatment of the cooking liquor can also advantageously be employed where it does not result in complete removal of carbon dioxide, but where it decreases the objectionable excess to a point which makes it unobjectionable, or which makes its removal easy during the cooking operation.

We claim:

1. The method of producing pulp, which comprises treating wood, at an elevated temperature, with a liquor containing a sulfite of sodium and both sodium carbonate and sodium bicarbonate in sufficient quantities to render the wood fibers readily separable.

2. The method of producing pulp, which comprises treating wood, at an elevated temperature, with a liquor containing a sulfite of sodium and both sodium carbonate and sodium bicarbonate and discharging carbon dioxide during the treatment, said sulfite and said carbonate and bicarbonate being present in sufficient quantities to render the wood fibers readily separable.

3. The method of producing pulp, which comprises treating wood, at an elevated temperature, with a liquor containing a sulfite of sodium and a lesser amount of both sodium carbonate and sodium bicarbonate, the liquor containing a sufficient amount of such compounds to render the wood fibers readily separable.

4. The method of producing pulp, which comprises treating wood, at an elevated temperature, with a liquor containing a sulfite of sodium and a lesser amount of both sodium carbonate and sodium bicarbonate and discharging carbon dioxide during the treatment, the liquor containing a sufficient amount of such compounds to render the wood fibers readily separable.

5. The method of producing chemical pulp from wood, which comprises subjecting the wood to a cooking operation, under pressure and at an elevated temperature, with a cooking liquor regenerated from residual liquor of the process and containing reactive sodium compounds of which sodium monosulfite is its primary reagent, and also containing a carbonate of sodium, the amount of such reactive sodium compounds being sufficient to maintain the cooking liquor alkaline to litmus during the cooking operation, and permitting carbon dioxide to escape during the cooking operation.

6. The process of producing pulp from wood, which comprises treating the wood, at an elevated temperature, with a liquor containing sodium sulfite as its principal reagent and also containing a carbonate of sodium, separating the residual liquor, concentrating the residual liquor and subjecting the product to a carbonizing or smelting treatment, forming a water solution of the sodium compounds contained in the product of the carbonizing or smelting treatment, treating the resulting solution to form a liquor containing sodium sulfite as its principal reagent and also containing a carbonate of sodium, and treating wood with the resulting liquor.

7. The process of producing pulp from wood, which comprises treating the wood, at an elevated temperature, with a liquor containing sodium sulfite as its principal reagent and also containing a carbonate of sodium, relieving carbon dioxide as the treatment progresses, separating the residual liquor, concentrating the residual liquor and subjecting the product to a carbonizing or smelting treatment, forming a water solution of the sodium compounds contained in the product of the carbonizing or smelting treatment, treating the resulting solution to form a liquor containing sodium sulfite as its principal reagent and also containing a carbonate of sodium, and treating wood with the resulting liquor.

8. The process of producing pulp from wood, which comprises treating the wood, at an elevated temperature, with a liquor containing sodium sulfite as its principal reagent and also containing a carbonate of sodium, separating the residual liquor, concentrating the residual liquor and subjecting the product to a carbonizing or smelting treatment, forming a water solution of the sodium compounds contained in the product of the carbonizing or smelting treatment, treating the resulting solution to form a liquor containing sodium sulfite as its principal reagent and also containing a carbonate of sodium, removing some carbon dioxide present in a free or loosely combined form, and treating wood with the resulting liquor.

9. The process of producing pulp from wood, which comprises treating the wood, at an elevated temperature, with a liquor containing sodium sulfite as its principal reagent and also containing a carbonate of sodium, relieving carbon dioxide as the treatment progresses, separating the residual liquor, concentrating the residual liquor and subjecting the product to a carbonizing or smelting treatment, forming a water solution of the sodium compounds contained in the product of the carbonizing or smelting treatment, treating the resulting solution to form a liquor containing sodium sulfite as its principal reagents and also containing a carbonate of sodium, removing some carbon dioxide present in a free or loosely combined form, and treating wood with the resulting liquor.

10. The improvement in the production of cooking liquors containing sodium sulfite and a carbonate of sodium, which comprises treating a solution containing a carbonate of sodium to convert some of the carbonate of sodium into a sulfite of sodium, and treating the solution to remove some of the carbon dioxide present in a free or loosely combined form.

11. The improvement in the production of cooking liquors containing sodium sulfite and a carbonate of sodium, which comprises treating a solution containing a carbonate of sodium with a reactive sulfite to convert some of the carbonate of sodium into a sulfite of sodium, and treating the solution to remove some of the carbon dioxide present in a free or loosely combined form.

12. The improvement in the production of a cooking liquor containing sodium monosulfite for use in the production of chemical pulp from wood, which comprises sulfiting a solution containing a carbonate of sodium with a reactive sulfite thereby forming a liquor containing a sulfite of sodium and some carbon dioxide in a free or loosely combined state, and heating the sulfited solution to drive off some of such carbon dioxide.

13. The improvement in the production of sodium monosulfite cooking liquors, which comprises subjecting a solution containing a carbonate of sodium, produced by treatment of the residual liquors of the process, to a sulfiting treatment with a reactive sulfite thereby forming a liquor containing a sulfite of sodium and some carbon dioxide in a free or loosely combined state, the sulfiting treatment being conducted at an elevated temperature.

14. The improvement in the production of cooking liquors containing sodium monosulfite, which comprises subjecting a solution containing sodium carbonate and sodium sulfid, produced by treatment of the residual liquors of the process, to a sulfiting treatment with a reactive sulfite at an elevated temperature.

15. The improvement in the production of cooking liquors containing sodium monosulfite as

the primary reagent, which comprises subjecting a solution containing sodium carbonate to sulfiting with a reactive sulfite and treating the solution with calcium hydroxide, whereby some calcium carbonate is formed.

16. The improvement in the production of cooking liquors containing sodium monosulfite in preponderating amount, which comprises subjecting a solution containing sodium carbonate and a lesser amount of sodium sulfid to a sulfiting treatment with a reactive sulfite, thereby forming a cooking liquor containing a preponderating amount of sodium sulfite.

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