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LINN BRADLEY, OF MONTCLAIR, NEW JERSEY, AND EDWARD P. McKEEFE, OF PLATTSBURGH, NEW YORK, ASSIGNORS TO BRADLEY-McKEEFE CORPORATION, OF NEW YORK, N. Y., A CORPORATION OF NEW YORK.

TREATMENT OF RESIDUAL LIQUOR.

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This invention relates to the treatment of the residual liquors from the production of wood pulp with a cooking liquor containing sodium monosulfite, or a mixture of sodium monosulfite and caustic soda.

In certain companion applications we have described a new and useful method of producing wood pulp from wood by subjecting the wood to a cooking operation, under pressure and at an elevated temperature, with a cooking liquor consisting essentially of sodium monosulfite, or sodium monosulfite together with a limited amount of caustic soda. Such processes result in the production of increased yields of a superior and improved pulp, containing fibers of great strength, which have not been objectionably injured by the cooking operation.

The present invention relates to the treatment of the residual liquors from such processes, whereby the processes may be made regenerative or cyclic in character.

The residual liquors produced by such pulp processes are of distinctive and characteristic composition. They contain a decreased content of organic matter, as compared with the black liquor from the soda or sulfate process, due to the fact that incrusting and non-fibrous constituents are dissolved or removed from the wood without dissolving or removing any considerable amount of the fibers themselves, whereas, in the soda and sulfate processes, a considerable amount of the fibers is dissolved and goes into the residual liquor.

The composition of the residual liquors which are treated according to the present invention will vary somewhat with different woods, and with the particular composition of the cooking liquor. With deciduous woods, such as poplar, basswood, maple, birch, beech, oak, etc., and with certain coniferous woods, such as spruce, pines, etc. the cooking operation may be carried out with a cooking liquor containing essentially normal sodium sulfite. With other woods, particularly highly resinous woods, such as certain pines, the cooking liquor may contain a sufficient amount of caustic soda, in addition to a preponderating proportion of sodium sulfite, so that the resinous and other incrusting and non-fibrous constituents will be removed from the fibers with substantial completeness, without, however, injuring the fibers themselves to any material degree.

In addition to sulfite, alkali and resinous or other encrusting and non-fibrous constituents, the liquor frequently contains sodium carbonate and some sodium acetate, sodium "resinates" and some sodium sulpho-organic compounds. The liquor may contain soaps or materials of a similar character resulting from the combination of the sodium sulfite or caustic soda or both with saponifiable constituents of the wood treated, particularly in the case of resinous woods where resin soaps or compounds of a similar character may be formed in considerable amounts. It may also contain tanning material, dyes and other dissolved organic material.

The residual liquor is usually mahogany in color, but the color varies somewhat in intensity with different woods and is somewhat darker when small amounts of caustic are used. In reaction the liquor is alkaline to litmus but not strongly alkaline unless caustic has been employed, the degree of alkalinity obviously depending upon the amount of caustic used.

In consistency the residual liquor may be thinner than black liquors commonly obtained by soda and sulfate processes, and it may contain a smaller proportion of solids in solution because the cellulose is not attacked and dissolved by sodium sulfite to any great extent during the pulp-making operation.

One purpose of the present invention is the recovery of valuable constituents of the residual liquor, particularly the sulfite radical and sodium content, so that these are consequently made available for the treatment of further quantities of wood.

According to the present invention, the residual liquor is treated in a relatively simple manner for the recovery of the more important constituents while the organic materials are destroyed. The residual liquor may thus be evaporated to dryness and the solids may be calcined or burned to produce sodium carbonate together with more or less sodium sulfite, etc. These compounds may then be dissolved from the insoluble carbon and treated with sulfur dioxide or sodium bisul-

fite or both to eliminate carbon dioxide. A product containing sodium sulfite or a mixture of sodium sulfite and sodium bisulfite may thus be obtained. Alternatively, some of the carbonate may be converted into caustic soda and used as such by addition thereof to the sodium sulfite liquor when a caustic liquor is needed.

When the residual liquor from the cooking of wood with sodium mono-sulfite or a mixture containing a preponderating amount of sodium monosulfite and a smaller amount of caustic soda is calcined, for example, in a rotary furnace such as is used in the calcination of the concentrated residual liquors of the ordinary soda process, a considerable decomposition of the sodium sulfite or sulfurous acid combinations contained in the liquors and in the dried product undergoing calcination, takes place, and a considerable amount of sulfur compounds escapes with the gaseous products of combustion by which the rotary calcining furnace is heated. In such cases the calcined product will contain a relatively large amount of sodium carbonate while it may still contain varying amounts of sodium sulfite. This method of forming sodium carbonate forms the subject of our application Serial No. 513,161, filed November 5, 1921.

When the calcined product is leached to give a solution containing sodium carbonate and varying amounts of sodium sulfite, this liquor may advantageously be used for recovering sulfur dioxide from the gases of the calcination. The gases from the rotary calcining furnace can, for example, be passed through an absorption tower through which the solution is passed, this absorption tower being arranged between the rotary calcining furnaces and the stack, and the necessary draft and circulation of the gases being secured by means of a fan. By using a tower or series of towers in this way, the sulfur dioxide of the escaping gases can be recovered for reuse in the process.

It is an advantage of this method of regenerating the sodium sulfite that it permits the use of ordinary calcining furnaces such as are available in pulp mills operating according to the ordinary soda process, and requires merely the insertion of absorption towers and circulating fans between the rotary furnaces and the stack, and the circulation of the leach liquors through the absorption towers. The treatment of the residual liquors can otherwise be carried out in the same apparatus and with similar manipulation as in the ordinary soda process, although the procedure with the residual liquors, according to the present invention, will have an entirely different result owing to the inherent differences in the residual liquor itself and in the reactions which take place during its treatment. The treatment of the residual liquors, in the manner described, results in the recovery of the greater part of the sodium content as well as of the sulfur dioxide content in the form of sodium sulfite in solution available for further use in the cooking operation.

The residual liquors produced from the cooking of dense hard woods (for example, birch, beech and maple) may have a radically increased content both of organic constituents and of inorganic matter, such as combined sodium organic compounds and sulfo-organic compounds. Residual liquors of such increased concentration will be somewhat diluted by admixture with wash waters, but dilution to an objectionable degree can be readily prevented, and the treatment of the more concentrated liquors presents added advantage because of the decreased amount of water to be remvoed and the radically increased concentration of the constituents which the liquor contains.

The regenerative process of the present invention permits of making the pulp process a cyclic operation in which sodium sulfite, with or without caustic soda, is employed as a cooking liquor in the production of pulp, with regeneration of the chemicals for further use in the cyclic process. In carrying out the cyclic operation, the cooking of the wood chips can be carried out, for example, in the manner more fully described in our prior application, Serial No. 481,147, filed June 28, 1921. When the pulp making process of said application is combined with the regeneration of the cooking liquor, or of ingredients of the cooking liquor, from the residual liquors, in the manner hereinbefore described, the pulp making process becomes a regenerative pulp process of a particularly advantageous character, enabling the pulp mill to operate with the treatment of the residual liquors and the regeneration of the cooking liquors in a particularly advantageous manner.

The losses of sodium can be made up by adding sodium carbonate or soda-ash and combining it with sulfur dioxide. The sulfur dioxide can be supplied to the necessary extent by simple sulfur burners and by absorption of the gases in alkaline solutions either of soda-ash or of residual liquors, or of leach liquors resulting from the calcination operations above described. The amount of sodium sulfite or of sodium sulfite and caustic soda regenerated from the residual liquors can be supplemented by the necessary additions to give a new cooking liquor suitable for further use in the process.

The regenerative or cyclic process of pulp manufacture, accordingly, presents important advantages in the manufacture of the pulp itself as set forth more fully in our said prior application as well as in the treatment of the residual liquors in the manner

herein described. We do not, however, claim the regenerative pulp process in the present application inasmuch as this forms the subject matter of a separate application.

It will thus be seen that the present invention provides an improved process of treating residual liquors for the recovery therefrom of a cooking liquor containing mainly sodium sulfite, either with or without caustic soda, and either with or without varying amounts of other sodium salts. This process involves the concentration of the residual liquors and the calcination of the concentrated product. The calcination is carried out under such conditions that a considerable decomposition of the sodium sulfite or sulfurous acid combinations contained in the liquors and in the dried products undergoing calcination takes place, and a considerable amount of sulfur compound escapes with the gaseous products of combustion from the calcining furnace. The calcined product, accordingly, will contain a relatively large amount of sodium corbonate, while it may nevertheless still contain varying and appreciable amounts of sodium sulfite. This product, when leached, will give a solution containing sodium carbonate and varying amounts of sodium sulfite. To the extent that the sodium sulfite is thus directly recovered, the production of further amounts of sodium sulfite is obviated. The gases given off during the calcination will contain considerable amounts of sulfur dioxide, as above pointed out, and the solution leached from the calcined product may advantageously be used for recovering sulfur dioxide from such gases of the calcination. In this way, a considerable amount of sulfur dioxide can be recovered in the form of sodium sulfite for reuse. This recovery of sodium sulfite for reuse thus involves a concentration and calcination of the constituents of the residual liquor, with driving off of a considerable amount of sulfur dioxide therefrom during the calcination, but with retention of part of the sulfur dioxide as sodium sulfite in the calcined product, and the recovery of sulfur dioxide from the gases escaping during the calcination in the solution leached from the calcined product.

This recovery process, in which the sulfite radical of the sodium sulfite initially employed is recovered in part directly as sodium sulfite from the calcined product, and in part by absorbing sulfur dioxide from the calcination gases in the solution leached from the calcined product, enables the rotary calcining furnaces of the ordinary soda process to be employed with simple additional equipment for the scrubbing of the gases with the leached liquor to recover sulfur dioxide as sodium sulfite.

In order to make up for losses of sulfur dioxide, sulfur dioxide from another source may be used for treating the solution leached from the calcined product; or sodium bisulfite can be used, in which case additional sodium will also be supplied. The treatment of the leached liquor with sulfur dioxide or with sodium bisulfite will result in decomposing most or all of the sodium carbonate, setting free and driving off carbon dioxide, and forming sodium sulfite.

Where the composite liquor is to contain caustic soda as well as sodium sulfite, some of the sodium carbonate may, as above stated, be causticized and converted into caustic soda and used as such by addition thereof to the sodium sulfite liquor otherwise regenerated or produced.

My invention may also be used with residual liquor which results from cooking wood with a cooking liquor containing sodium bisulfite.

This application contains subject matter disclosed in our co-pending applications Serial No. 513,761 and Serial No. 534,768, the latter having issued as Patent No. 1,637,515.

We claim:

1. The method of producing a cooking liquor from the residual liquor resulting from the cooking of wood with a cooking liquor containing essentially sodium sulfite or sodium sulfite and caustic alkali, which comprises evaporating such liquor to dryness, calcining the dried product under conditions to drive sulfur compounds therefrom and to give a calcined product containing a relatively large amount of sodium carbonate, and also containing some sodium sulfite, leaching the calcined product, and sulfiting the same to convert sodium carbonate to sodium sulfite.

2. The method of treating residual liquor from the production of pulp with a cooking liquor containing sodium sulfite or sodium sulfite and caustic soda, which comprises evaporating the residual liquor to dryness, calcining the dry product without smelting the same, dissolving the sodium salts from the calcined product, and subjecting the solution to the action of the sulfite radical to convert sodium carbonate into sodium sulfite.

3. The method of treating residual liquor from the production of pulp with a cooking liquor containing sodium sulfite or sodium sulfite and caustic soda, which comprises evaporating the residual liquor to dryness, and subjecting the same to calcination under conditions to drive off sulfur compounds therefrom and to give a calcined product containing a relatively large amount of sodium carbonate and also containing sodium sulfite.

4. The process of producing a cooking liquor containing sodium sulfite which comprises digesting wood with a cooking liquor containing essentially sodium sulfite or sodium sulfite and caustic soda, separating the resulting liquor from the cooked wood, con-

centrating the resulting liquor, subjecting the concentrated liquor to calcination without smelting the same, extracting the calcined product, and treating the resulting solution with sulfur dioxide or a compound containing the sulfite radical, with resulting conversion of sodium carbonate to sodium sulfite.

5. The method of producing a cooking liquor containing caustic soda, sodium sulfite and sodium thiosulfate, which comprises evaporating a residual liquor from the cooking of wood with a cooking liquor containing caustic soda and sodium sulfite, calcining the concentrated product without smelting to give a calcined product containing sodium carbonate and sodium-sulfur compounds, including three element compounds, leaching the calcined product, and treating the leached liquor to convert part of the sodium carbonate into caustic soda and to form sodium sulfite.

6. The method of producing a cooking liquor from the residual liquor resulting from the cooking of wood with a cooking liquor containing essentially sodium sulfite or sodium sulfite and caustic alkali, which comprises evaporating such liquor to dryness, calcining the dried product under conditions to drive sulfur compounds therefrom and to give a calcined product containing a relatively large amount of sodium carbonate, and also containing some sodium sulfite, leaching the calcined product, and subjecting the leach liquor in part to causticizing to convert sodium carbonate into caustic soda and in part to sulfiting to convert sodium carbonate into sodium sulfite.

7. The method of treating residual liquor from the production of pulp with a cooking liquor containing sodium sulfite or sodium sulfite and caustic soda, which comprises evaporating the residual liquor to dryness, calcining the dry product in a furnace under conditions to form sulfur dioxide therefrom and to give a calcined product containing a relatively large amount of sodium carbonate, leaching the calcined product, and absorbing the sulfur dioxide formed during the calcination in such solution.

8. The method of treating residual liquor from the production of pulp with a cooking liquor containing sodium sulfite or sodium sulfite and caustic soda, which comprises evaporating the residual liquor to dryness, calcining the dry product in a furnace under conditions to form sulfur dioxide therefrom and to give a calcined product containing a relatively large amount of sodium carbonate, absorbing the sulfur dioxide formed during the calcination in a solution of sodium carbonate and thereby forming sodium sulfite for further use in the cooking liquor.

9. The process of producing a cooking liquor containing sodium sulfite which comprises digesting wood with a cooking liquor containing essentially sodium sulfite or sodium sulfite and caustic soda, separating the resulting liquor from the cooked wood, concentrating the resulting liquor, subjecting the concentrated liquor to calcination without smelting the same, extracting the calcined product, and treating the resulting solution in part with sulfur dioxide or a compound containing the sulfite radical to convert sodium carbonate into sodium sulfite, and in part by causticizing with lime to form caustic soda.

10. The method of treating residual liquor from the production of pulp with a cooking liquor containing sodium sulfite which comprises evaporating the residual liquor to dryness, calcining the dry product without smelting the same, dissolving the sodium salts from the calcined product, and subjecting the solution to the action of the sulfite radical to convert sodium carbonate into a mixture of sodium sulfite and sodium bisulfite.

11. The method of treating residual liquor from the production of pulp with a cooking liquor containing sulfite of sodium which comprises evaporating the residual liquor to dryness, subjecting the dry material to a furnacing operation under conditions to drive off sulfur compounds with the furnace gases in sufficient quantity to give a furnace product containing a relatively large amount of sodium carbonate and also containing sodium-sulfur compounds and treating such furnace product for the production of a cooking liquor containing sulfite of sodium, the sodium content of such sulfite being derived in part from such sodium-sulfur compounds and in part from the carbonate of sodium.

12. In a process for regenerating cooking liquor, the steps which include digesting cellulose-bearing material by means of cooking liquor which includes a substantial amount of a sulfite of an alkali-metal and continuing the digesting treatment until fibres thereof are readily separable from each other by mechanical treatment, separating resulting residual liquor from resulting fibrous material, removing water from residual liquor, furnacing the residue under conditions adapted to yield a furnace product including alkali-metal carbonate and alkali-metal sulfur-bearing compounds, and forming a cooking liquor including a sulfite of an alkali-metal, the alkali-metal content of such sulfite being derived in part from such alkali-metal carbonate and in part from such alkali-metal sulfur-bearing compounds.

13. In a process for regenerating cooking liquor, the steps which include digesting cellulose-bearing material by means of cooking liquor which includes a substantial amount of a sulfite of an alkali-metal and continuing the digesting treatment until fibres thereof are readily separable from

each other by mechanical treatment, separating resulting residual liquor from resulting fibrous material, removing water from residual liquor, furnacing the residue under conditions adapted to yield a furnace product including a preponderating amount of alkali-metal carbonate and a lesser amount of alkali-metal sulfur-bearing compounds, and forming a cooking liquor including a sulfite of an alkali-metal, the alkali-metal content of such sulfite being derived in part from such alkali-metal carbonate and in part from such alkali-metal sulfur-bearing compounds.

14. The method of treating residual liquor from the production of pulp with a cooking liquor containing a sulfite of sodium, which comprises evaporating the residual liquor to dryness, burning the organic matter therein, forming a solution containing sodium salts derived from the resulting product, said sodium salts including a carbonate of sodium and a sodium-sulfur compound, and subjecting the solution to the action of sulfur dioxide by passing the solution over a tower and passing sulfur-dioxide-bearing gases through the tower to absorb sulfur-dioxide in the liquor.

15. In a process for regenerating a cooking liquor, the steps which include digesting wood by means of a cooking liquor supplied with about 30% to 40% of sodium monosulfite (Na_2SO_3), based on the air-dried weight of the wood, and digesting until the wood fibres are substantially freed from non-fibrous constituents, separating resulting residual liquor from resulting fibrous material, removing water from such residual liquor, furnacing the residue under conditions adapted to form furnace gases which carry the greater amount of the sulfur present in such cooking liquor as sodium monosulfite when charged into the digester and under conditions adapted to yield a furnace product including sodium compounds of which a preponderating amount is sodium carbonate and a lesser amount is sodium-sulfur compounds, forming therefrom a cooking liquor including sulfite of sodium derived from sodium compounds contained in such furnace product, the sodium content of such cooking liquor being derived in part from a carbonate of sodium and in part from the sodium-sulfur compounds.

16. The method of treating residual liquor from the production of pulp with a cooking liquor containing a sulfite of sodium which comprises evaporating the residual liquor to dryness, subjecting the dry material to a furnacing operation under conditions to drive off sulfur compounds with the furnace gases in sufficient quantity to give a furnace product containing a relatively large amount of sodium carbonate and also containing sodium-sulfur compounds and treating such furnace product by means of a sulfite radical for the production of a cooking liquor containing sulfite of sodium, the sodium content of such sulfite being derived in part from such sodium-sulfur compounds and in part from the carbonate of sodium, the treatment of the sulfite radical being continued until substantially all of the carbonate of sodium has reacted therewith.

17. The method of treating residual liquor from the production of pulp with a cooking liquor containing a sulfite of sodium which comprises evaporating the residual liquor to dryness, subjecting the dry material to a furnacing operation under conditions to drive off sulfur compounds with the furnace gases in sufficient quantity to give a furnace product containing a relatively large amount of sodium carbonate and also containing sodium-sulfur compounds and treating such furnace product by means of a sulfite radical recovered from the furnacing operation for the production of a cooking liquor containing sulfite of sodium, the sodium content of such sulfite being derived in part from such sodium-sulfur compounds and in part from the carbonate of sodium.

In testimony whereof we affix our signatures.

LINN BRADLEY.
EDWARD P. McKEEFE.