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## PRODUCTION OF PULP

No Drawing. Original application filed February 7, 1922, Serial No. 534,768. Divided and this application filed July 2, 1927. Serial No. 203,267.

This invention relates to a regenerative method for the production of wood pulp with a cooking liquor containing sodium monosulfite, or a mixture of sodium monosulfite and caustic soda, and with treatment of the residual liquors from such process for further use in the process.

In certain companion applications Serial Nos. 481,147 and 711,857 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 improvements in such processes, and to the treatment of the residual liquors from such processes, whereby the processes become 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, bass wood, 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 cer-

tain 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 sulphite, alkali and resinous or other incrusting 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 sulphite 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 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 sulphate processes, and it may contain a smaller proportion of solids in solution because the cellulose is not attacked and dissolved by sodium sulphite 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 sulphite radical and sodium content, so that these are consequently made available for the treatment of further quantities of wood. Incidentally, other valuable and useful products are recovered or made available.

Where a considerable excess of sodium sulphite is employed in the cooking liquor, the residual liquor may still contain considerable

of this material in a free state, and merely by concentrating the residual liquor some of the unconsumed sodium sulphite can be crystallized out upon the cooling. When the liquor is concentrated directly in this way, exposure to the air during concentration should be avoided as much as possible in order to prevent conversion of the sulphite into sulphate. This concentration may be employed as the preliminary step in the treatment of the residual liquor, the recovered sodium sulphite being immediately available for reuse while other valuable materials in the residual liquor are recovered by further treatment.

As a further preliminary step, a portion of the dissolved organic matter may be separated by treating the residual liquor with suitable acids, rendering it acid in reaction. The precipitated organic matter can then be filtered off, leaving a clear liquor containing a decreased content of dissolved organic matter and being thus more readily susceptible to further treatment for the recovery of the sulphite radical and sodium ion remaining therein.

For the further treatment of the residual liquor or for the treatment of such liquor without preliminary treatment as hereinbefore set forth, the addition of sulphur dioxide in quantities sufficient to convert sodium compounds into sodium sulphite affords an effective method of regenerating sodium sulphite for reuse as a cooking liquor. Following the treatment with sulphur dioxide, some organic matter present in the solution may be separated and the liquor is then ready for further use after the addition of sufficient sodium sulphite to make up the material consumed in the cooking operation. A portion of the sodium sulphite may be causticized by the addition of calcium hydroxide if the presence of caustic soda in the liquor is desirable.

Where considerable caustic soda has been employed in combination with the sodium sulphite, as in the treatment of certain woods, sulphur dioxide may be added, (together with sodium bisulphite, the latter being added in amount sufficient to make up the loss of soda), to combine with any unused caustic soda and to displace some of the organic-acid radicals, thus increasing the yield of sodium sulphite. If the organic radical released is insoluble in the neutral or acid liquor, as for example, the "resins", "gums", etc., a considerable amount of sodium sulphite may be recovered from sodium organic compounds present in the liquor. Thus the residual liquor from the cooking of resinous woods, such as spruce (and especially pines) contain sodium organic compounds which may be converted into sodium sulphite by treatment with sulfur dioxide. Following the treatment described, the liquor may be clarified and causticized to the desired degree by

the addition of calcium hydroxide. Any calcium sulphite resulting from the addition of calcium hydroxide in the causticizing operation may be converted into calcium sulphate by treatment with sodium sulphate in the presence of free acid, e. g., sulphurous acid.

The residual liquors frequently contain some sodium in combination with organic acid radicals, such as the acetate, etc., which acids either displace sulphurous acid from sodium sulphite or are volatile when set free, and which are more or less soluble in the presence of sulphur dioxide. In actual practice, therefore, it may be advantageous to provide for the conversion of the sodium of these organic compounds, which otherwise might concentrate in the liquor to an objectionable degree, into sodium sulphite or sodium acid sulphite, and to remove the separated acids or acid compounds. It may not be essential, however, that organic compounds of this character be removed after every cooking operation since the accumulation may not be sufficient to prevent satisfactory reuse of the liquor. It is sufficient in such cases if the organic compounds are decomposed and removed either wholly or in part after two or more cooking operations.

When the residual liquor contains sufficient organic matter to interfere with further use thereof in whole or in part as a cooking liquor, the liquor may be treated while neutral or alkaline with gypsum (calcium sulphate) which will react with the sodium sulphite and precipitate calcium sulphite, leaving sodium sulphate in solution. In this manner, substantially all of the sulphite radical existing as sodium sulphite can be precipitated from the liquor. Preferably a slight excess of gypsum is employed to insure complete precipitation. This precipitation may be carried out either before or after concentration of the residual liquor and the solution containing the sodium sulphate may be concentrated to a greater or less degree. So long as the solution is slightly alkaline or neutral, the calcium sulphite will be precipitated without any appreciable occlusion of organic matter, and the organic matter will thus remain in solution with sodium sulphate. The precipitated calcium sulphite may be removed from the liquor by filtration, decantation, sedimentation or otherwise. Thus it may be permitted advantageously to settle so that the liquor may be drawn off, leaving the calcium sulphite for further use as hereinafter described.

The solution containing the sodium sulphate and organic matter may be concentrated by evaporation or otherwise until the greater portion of the sodium sulphate crystallizes out on cooling. Further concentration of the liquor occurs because of the water taken up as water of crystallization by

the sodium sulphate. Some gypsum will crystallize with the sodium sulphate but this is unobjectionable. The organic matter will be left in the solution after crystallization of the sodium sulphate therefrom and some may be removed by further concentration or by acidification and separation of the resulting precipitate.

The crystallized sodium sulphate may be dissolved, preferably in wash water from the washing of the pulp, and added to the calcium sulphite precipitate produced as above described. If an acid such as sulphuric acid or nitre cake (acid sodium sulphate) or an excess of sulphur dioxide is then added, the calcium sulphite will react with the sodium sulphate, precipitating gypsum and leaving sodium sulphite in solution. The use of nitre cake as an acidifying agent is desirable inasmuch as the sodium of the nitre cake is thus added to the liquor, making up any losses of sodium in the process. The acid solution may be neutralized with calcium hydroxide, thus producing a further precipitate of calcium sulphite. The gypsum may be separated from the liquor by filtration, decantation, sedimentation or otherwise and utilized again in the treatment of further amounts of residual liquor.

The solution of sodium sulphite obtained as above, with proper regulation of its concentration, is ready for reuse as a cooking liquor. If a cooking liquor is desired containing caustic in addition to sodium sulphite, the liquor may be causticized to the desired degree by treatment with calcium hydroxide.

Instead of concentrating the sodium sulphate solution and crystallizing the sodium sulphate therefrom, this solution may be concentrated and acidified to precipitate part of the organic matter, and the resulting clear solution may then be treated with the calcium sulphite precipitate to regenerate sodium sulphite in acid solution with precipitation of gypsum which may be separated from the solution. The excess acid used for acidifying the liquor assists in bringing about the reaction of sodium sulphate and calcium sulphite, or a further amount of acid may be added if necessary.

It will be noted that the process as described involves the treatment of the residual liquor with calcium sulphate while the liquor is neutral or alkaline with resulting reaction of the calcium sulphate and sodium sulphite to give a precipitate of calcium sulphite and a solution of sodium sulphate. This sodium sulphate solution, after the separation of organic matter therefrom, is caused to react with the calcium sulphite in the presence of a sufficient amount of the acid to reproduce the sodium sulphite in solution with precipitation of calcium sulphate. The direction of the reaction thus depends upon

whether the solution is alkaline or acid. The calcium sulphate and calcium sulphite used as reagents are continuously regenerated so that it is necessary only to add a sufficient amount of these materials from time to time to make up for losses. When lime is used for neutralizing the acidity, or nitre cake or sodium bisulphate to give the necessary acidity, they also serve to make up any losses of calcium and of sodium in the process.

The concentrated mother liquor after crystallization of the sodium sulphate therefrom has marked saponaceous properties and can be used as a soap or soap ingredient for industrial purposes, or for the production of tanning material and dye stuffs. When the liquor is acidified, organic matter is precipitated in a flocculent condition and the mahogany color of the liquor is destroyed although this color reappears if the liquor is subsequently made alkaline. The liquor obtained from resinous woods such as pine, when a small amount of caustic alkali is used with the sodium sulphite during the cooking operation, contains a correspondingly increased content of resin soaps and similar materials, and such liquors, after concentration, will contain correspondingly increased amounts of saponaceous material which can be recovered therefrom.

If nitre cake alone is used to form sodium sulphate from the sodium-organic compounds, volatile acids such as acetic, formic, etc., may be set free and removed by heat treatment. Insoluble organic compounds may be removed by filtration, sedimentation or otherwise, and the solution of sodium sulphate may be concentrated, e. g., by evaporation and cooling to obtain crystals of sodium sulphate which are free from an objectionable amount of organic matter. If the mother liquor from the sodium sulphate crystallization contains considerable sodium sulphate and organic matter, the organic matter may be charred after evaporation of the liquor and preferably without reduction of the sodium sulphate to sodium sulphide. The sodium sulphate may then be dissolved out of the charred and insoluble materials. This sodium sulphate may be added to that obtained by crystallization.

If desired, some of the sodium-organic compounds may be decomposed and converted into sodium carbonate. Any sodium sulphide obtained may also be decomposed to release hydrogen sulphide which may be removed by heat treatment and burned to recover the sulphur dioxide employed in the process. In some cases, the presence of sodium sulphide in the cooking liquor may not be objectionable, and, in such cases, such amounts of sodium sulphide as are present need not be decomposed.

Any sodium carbonate or sodium carbonate with sodium sulphide or sulphite which is re-

covered in the process may be causticized with lime and the caustic produced can be added to the sodium sulphite liquor in case a caustic liquor is desired, or the sodium carbonate can be treated with sulphurous acid to form sodium sulphite. The sodium carbonate may thus be used to neutralize uncombined sulphurous acid in the solution of sodium sulphite instead of using calcium carbonate or hydroxide. This procedure insures the return of the sodium ion to the solution.

Under certain circumstances, a portion only of the residual liquor need be converted to produce sodium sulphite when nitre cake is used for the elimination of organic matter from the cycle. The remainder of the sodium organic compounds may be disposed of in any expedient manner. Acetic acid, sodium acetate, etc. may be recovered therefrom and tanning materials, dye stuffs, etc. may also be recovered when the residual liquors contain such constituents.

It may be desirable to eliminate certain steps of the process as hereinbefore set forth and to treat the residual liquor in a relatively simple manner for the recovery of the more important constituents while the organic materials are destroyed. Thus the residual liquor may be evaporated to dryness and the solids may be calcined or burned to produce sodium carbonate with more or less sodium sulphite, sulphide, etc. These compounds may then be dissolved from the insoluble carbon and treated with sulphur dioxide or sodium bisulphite or both to eliminate carbon dioxide and hydrogen sulphide. A product containing sodium sulphite or a mixture of sodium sulphite and sodium bisulphite 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 sulphite liquor when a caustic liquor is needed.

When the residual liquor from the cooking of wood with sodium mono-sulphite or a mixture containing a preponderating amount of sodium monosulphite 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 sulphite or sulphurous acid combinations contained in the liquors and in the dried product undergoing calcination, takes place, and a considerable amount of sulphur 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 sulphite. This method of producing sodium carbonate from sodium sulphite is described more fully in our prior application, Serial No. 513,161, filed Nov. 5, 1921.

When the calcined product is leached to give a solution containing sodium carbonate and varying amounts of sodium sulphite, this liquor may advantageously be used for recovering sulphur 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 sulphur dioxide of the escaping gases can be recovered for reuse in the process. It is an advantage of this method of regenerating the sodium sulphite 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 sulphur dioxide content in the form of sodium sulphite in solution available for further use in the cooking operation.

The residual liquors treated will, as above stated, vary in their composition and properties with different kinds of wood. With dense hard woods (for example birch, beech and maple) which have a considerably greater weight than poplar wood, the total amount of wood charged into a digester will be a great deal more than the weight of poplar wood commonly chargeable into the same digester. The amount of non-fibrous constituents which such dense hard woods contain and which must be removed by the cooking operation, will be radically greater than in the case of a digester of poplar wood. The amounts of such non-fibrous constituents in such woods is in fact so great that it is impracticable, with the ordinary soda process, to carry out a satisfactory cook, owing to the excessive strength and amount of the caustic soda in solution required for the treatment of a digester charge of chips, and the injury which caustic soda of the necessary increased strength has upon the pulp fibres desired. Such woods can nevertheless be satisfactorily cooked with a cooking liquor consisting es-

essentially of sodium mono-sulphite or sodium mono-sulphite with a limited amount of caustic soda, since the amount and concentration of these reagents in the cooking liquor can be increased to a degree which permits the satisfactory cooking of even the dense hard wood chips without objectionable injury thereto. The residual liquors produced from the cooking of such woods may have a radically increased content both of organic constituents and of inorganic matter, such as combined sodium organic compounds and sulpho-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 removed and the radically increased concentration of the constituents which the liquor contains.

In the foregoing we have described in detail the several operations whereby we are enabled to recover the chemicals required for the pulp-making operation from the residual liquors resulting from this operation, as well as the recovery of valuable by-products from the liquors. Obviously the details of the process are capable of numerous variations without departing from the invention, and we claim, therefore, the application of the broad principles of the invention as set forth herein. The procedure described eliminates the objectionable features which have characterized methods of recovering valuable products from pulp-cooking liquors as heretofore employed and is particularly advantageous inasmuch as it permits the practice of the pulp-making operations hereinbefore referred to at a relatively low cost because of the possibility of re-utilizing the chemicals employed with relatively slight additions to make up for inevitable losses in conducting these operations. It thus permits a cyclic operation in which sodium sulphite, with or without caustic soda, is employed as a cooking liquor in the production of pulp from various cellulose-containing materials and the regeneration and reuse of the sulphite liquor. This cyclic operation is a part of the invention herein described and claimed.

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.

Such losses of the ingredients as take place in the process can be made up, for example, in the manner above described. The losses of sodium can be made up by adding sodium carbonate or soda-ash and combining it with sulphur dioxide; or by adding sodium sulphate or salt cake or niter cake in the manner above described. The sulphur dioxide can be supplied to the necessary extent by simple sulphur burners and by absorption of the gases in alkaline solutions either or soda-ash or of residual liquors, or of leach liquors resulting from the calcination operations above described. The amount of sodium sulphite or of sodium sulphite 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.

This application is a division of our prior application Serial No. 534,768, filed February 7, 1922.

We claim:

1. The process which comprises cooking cellulosic fiber-bearing material in a solution containing sodium compounds, most of the sodium content thereof being in the form of a sulfite of sodium, subjecting residual liquor derived therefrom to a treatment including a furnacing step regulated to burn the combustible content of the residual liquor and to leave a non-gaseous furnace product including inorganic sodium compounds derived from the residual liquor, and passing products of combustion from such furnacing step in contact with other residual liquor from such a pulp-making operation for the recovery of soluble compounds therefrom.

2. The process according to claim 1, in which the solution used in the first named cooking step is alkaline to litmus and an alkaline residual liquor is used for absorbing soluble compounds from the products of combustion.

3. A process which comprises cooking raw cellulosic material in a solution that contains a sulfite of sodium; separating the pulp from the spent cooking liquor; furnacing the inorganic mineral content and burning the combustible content of such spent liquor; recovering resulting inorganic sodium compounds; and passing the products of combustion from such burning operation in contact with liquor that contains carbonate of

sodium derived from the inorganic mineral content by such furnacing operation, for the recovery of sulfur-bearing material from such products of combustion.

4. The process according to claim 3, in which the furnacing and burning treatment is carried out so as to produce a furnace product that contains sodium carbonate and a substantial but lesser amount of sodium sulfid; and in which such sodium compounds are dissolved to form an alkaline solution, and sodium carbonate thereof is used to recover sulfur dioxide from the products of combustion from such burning operation.

5. A process which comprises cooking cellulosic-fibre-bearing material in a cooking liquor that contains most of its sodium in the form of a sulfite of sodium; separating the spent cooking liquor from the resulting undissolved fibre-bearing material; evaporating water contained in the spent cooking liquor, furnacing solids derived from such liquor and burning combustible matter thereof so as to produce a non-gaseous furnace product that contains most of its sodium in the form of sodium carbonate; recovering the resulting sodium carbonate; and passing the products of combustion from such burning operation in contact with liquor that contains the resulting sodium carbonate to recover sulfur-bearing materials therefrom.

6. The process according to claim 5, in which the said non-gaseous furnace product contains both sodium carbonate and sodium sulfid.

7. The process according to claim 5, in which the said sodium carbonate is dissolved to form a solution and a solution that contains such recovered soda is used to recover sulfur dioxide from such products of combustion.

8. The process according to claim 5, in which sulfur dioxide is recovered from such products of combustion by means of liquor that contains carbonate of sodium and such recovered sulfur dioxide is employed as a sulfite of sodium in a subsequent cooking treatment of cellulosic-fibre-bearing material.

9. The process for producing pulp, which comprises cooking wood with cooking liquor that contains sodium in the form of a sulfite of sodium; removing residual liquor from undissolved fibre-bearing material; supplying to other wood and cooking such wood with cooking liquor that includes such residual liquor; removing a second residual liquor from undissolved fibre-bearing material; evaporating water contained in such second residual liquor; burning combustible matter derived from such second residual liquor so as to produce gaseous products of combustion which carry gaseous sulfur-bearing compounds and so as to recover a non-gaseous furnace product that contains most of its sodium in the form of sodium carbonate; preparing a

solution that contains such recovered sodium carbonate; subjecting such solution to a treatment including a sulfiting step so as to convert sodium carbonate thereof into a sulfite of sodium; and cooking wood with cooking liquor that contains such regenerated sulfite of sodium.

10. The process according to claim 9, in which the said non-gaseous furnace product contains both sodium carbonate and sodium sulfid and a sulfite of sodium is derived from each of these sodium compounds.

11. In a process for producing pulp from wood, the steps which comprise cooking wood in a cooking liquor supplied with a sulfite of sodium; evaporating water contained in the residual liquor; burning combustible matter derived from such residual liquor so as to produce a non-gaseous furnace product including sodium carbonate; dissolving such sodium carbonate and using the same in solution so as to recover sulfur dioxide from products of combustion of the burning step.

12. The process according to claim 11, in which the said non-gaseous furnace product contains both sodium carbonate and sodium sulfid, these two sodium compounds are dissolved and the resulting solution is used so as to recover sulfur-bearing matter from products of combustion of the burning step.

13. A process which comprises digesting cellulosic fibre-bearing material with a cooking liquor that contains a sulfite of sodium, separating a residual liquor from the fibre-bearing materials, passing such a residual liquor containing sulfite of sodium and a carbonate of sodium into contact with hereinafter-mentioned furnace gases to recover soluble sulfur compounds therefrom, burning combustible matter of the residual liquor so as to form sulfur-bearing furnace gases and a non-gaseous furnace product that contains carbonate of sodium, passing such furnace gases into contact with the solution above mentioned, dissolving sodium carbonate from the furnace product, forming a sulfite of sodium therefrom, and digesting cellulosic fibre-bearing material with liquor containing such regenerated sulfite of sodium.

14. A process according to the preceding claim, in which the first mentioned cooking liquor is non-acid to litmus and contains sodium sulfite and a sulfur-free sodium compound that is alkaline to litmus.

In testimony whereof we affix our signatures.

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