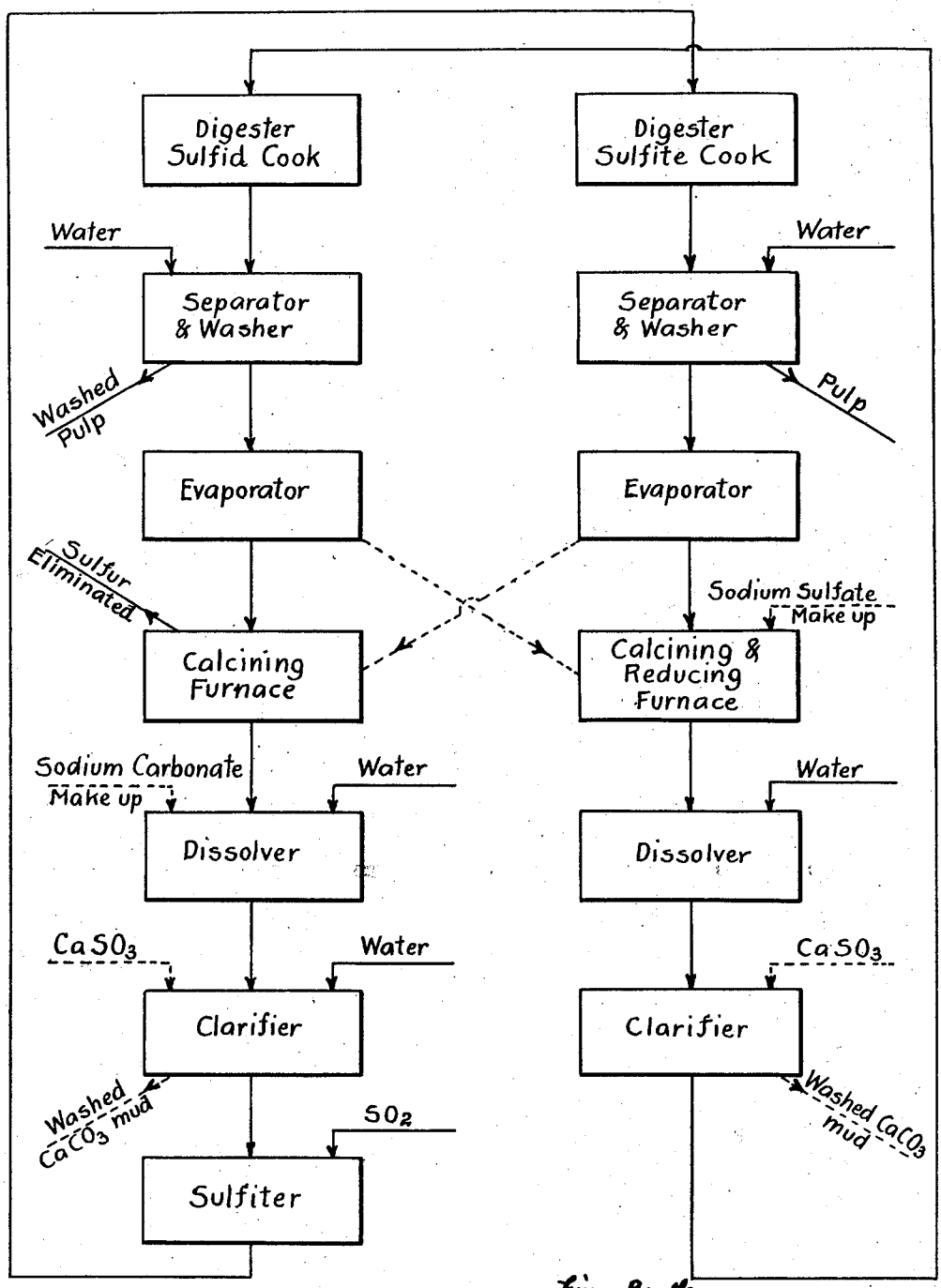
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MANUFACTURE OF PULP, ETC

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MANUFACTURE OF PULP, ETC.

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This invention relates to the production of wood pulp from wood and includes improvements in the cooking of wood with cooking liquors containing sodium sulfur compounds and improvements in the treatment of the residual liquors for the production of further amounts of cooking liquors therefrom.

More particularly, the invention includes improvements in inter-related cooking processes, wherein residual liquor from one process is utilized in whole or in part for the production therefrom of cooking liquor for the other process, and vice versa, the cooking liquors of both processes containing sodium sulfur compounds. The invention also includes improvements in the individual cooking processes as well as in the combination of the cooking process with the treatment of the residual liquors for the production of cooking liquor.

One of the cooking processes included in the invention is a cooking process in which the cooking liquor contains sodium monosulfite as a preponderating ingredient, the sodium monosulfite being used either alone or in admixture with other ingredients, such as sodium hydroxide, sodium sulfide, sodium carbonate, sodium thiosulfate, sodium sulfate, etc. Such processes are described in our prior applications Serial No. 481,147, filed June 28, 1921, Serial No. 686,137, filed January 14, 1924, Serial No. 704,176, filed April 4, 1924, Serial No. 57,953, filed September 22, 1925, of which applications the present application may be considered in part a continuation.

Another cooking process included in the present invention is one in which sodium sulfide is utilized as the main or predominating reactive constituent with which other constituents may be present, particularly sodium carbonate, or sodium sulfite, or sodium thiosulfate.

According to the present invention, the residual liquor from the sodium monosulfite cooking process is treated for the production therefrom of a cooking liquor for use in the sodium sulfide cooking process and the residual liquor from the sodium sulfide cooking process is treated for the production therefrom of a sodium monosulfite cooking liquor.

The residual liquor from the sodium monosulfite cooking process is subjected to concentration and the resulting product to a carbonizing and reducing treatment, such as a smelting operation, to produce a reduced product or melt containing a large amount of sodium sulfide. A solution is made of the sodium salts of the reduced product and this solution is utilized either without or advantageously after further treatment as a cooking liquor in the sodium sulfide cooking process.

The residual liquor from the sodium sulfide cooking process is concentrated and the resulting products subjected to a carbonizing treatment under suitable conditions (e. g. oxidizing) to remove a considerable amount of sulfur therefrom and to give a carbonized or incinerated product containing a preponderating amount of the soda as sodium carbonate with which some sodium sulfide or/and other sodium-sulfur compounds may also be present. A solution of the sodium salts of such a product is subjected to a sulfiting treatment to form a sodium sulfite cooking liquor.

In this interchanged cycle of operations, the sulfur and soda of the residual liquor from the sodium sulfite cooking process are employed to furnish sodium sulfide in the subsequent sulfide cooking operations and the treatment of residual liquor from the sodium sulfide cooking operation is utilized to eliminate sufficient sulfur and to convert the sodium content into compounds of an advantageous form readily utilizable after subsequent treatment in the sulfite cooking process.

The cooking liquor for the monosulfite process may be made up essentially of sodium monosulfite or it may have admixed therewith varying amounts of other sodium salts, such as sodium thiosulfate or sodium sulfide, for example, as described in our prior applications Ser. Nos. 704,176 and 57,953 hereinbefore referred to. The cooking liquor may also contain some sodium carbonate and we do not exclude the presence of small amounts

of caustic soda. Sodium sulfate may also be present. The cooking operation is carried out with a sufficient amount of cooking liquor and of chemicals therein in suitable ratio to produce chemical pulp and the residual liquor which contains the reaction products of the reactive chemicals with certain organic constituents of the wood.

The residual liquor from such a monosulfite cooking process is evaporated or concentrated, for example, in multiple-effect evaporators, or other suitable evaporators and the concentrated or evaporated product is subjected to a carbonizing and reducing or smelting operation under such conditions that a considerable part of the sodium-sulfur compounds are reduced to sodium sulfide in the furnace product or melt. In order to increase the sodium sulfide content of the furnace product sodium sulfate may be added, e. g. to the concentrated residual liquor before the furnacing operation, so that it will be subjected to reduction during the reducing or smelting operation. Calcining and smelting furnaces such as used in the so-called sulfate process are suitable for use in carrying out the reduction or smelting treatment of the present process.

As a result of this treatment the sodium content of the residual liquor is largely converted into sodium sulfide, while greater or less amounts of sodium carbonate may also be formed. Upon leaching or dissolving the furnace product or melt, a solution is obtained containing sodium sulfide and sodium carbonate as the principal sodium compounds, these two compounds being present in varying ratio, depending on the conditions of the treatment, but in general a high proportion of sodium sulfide is desirable.

The resulting solution, preferably after clarification, when adjusted as to concentration, can be utilized directly in the sodium sulfide cooking operation, so that the cooking liquor in such case will contain mainly sodium sulfide and sodium carbonate, although other compounds may be present with advantage. By utilizing a sufficient amount of sodium sulfide in the cooking liquor the wood can be satisfactorily cooked when the sulfide is accompanied by a considerable amount of sodium carbonate. The cooking operation can be carried out, for example, at a temperature of around 170° C. and at corresponding steam pressure and utilizing, for example, an amount of sodium sulfide equal to about 20–25% of the air-dry weight of the wood (e. g. wood containing 10% moisture). The amount of sulfide may vary with different kinds of wood, in general more sulfide being employed for resinous pulp woods than for deciduous pulp woods.

Instead of utilizing the untreated solution containing mainly sodium sulfide and sodium carbonate, it may advantageously be treated to convert some of the sodium carbonate into sodium sulfite, for example, by treating the solution with calcium sulfite, which will react with sodium carbonate to form calcium carbonate and sodium sulfite. In such case the cooking liquor may be made up mainly of sodium sulfide and sodium sulfite, with some sodium carbonate, in case all of the sodium carbonate is not converted into sulfite, and other sodium compounds.

When the solution is sulfited in this way, the calcium sulfite utilized therefor can be formed by burning sulfur in a sulfur burner and causing resulting sulfur dioxide to react with lime or calcium carbonate. The precipitated calcium carbonate formed by the sulfiting operation in which Na_2CO_3 is converted into Na_2SO_3, may be resulfited for reuse, but it should be sufficiently washed to remove sodium sulfide before resulfiting, to form more $CaSO_3$.

The sulfiting of the Na_2CO_3—Na_2S liquor can be advantageously carried out with agitation of the solution with the required amount of finely divided calcium sulfite, and the sulfiting of the calcium carbonate with sulfur dioxide can advantageously be carried out with agitation of a suspension of precipitated calcium carbonate in a solution of sulfurous acid or in water to which sulfur dioxide is introduced; or such calcium carbonate or lime can be added to a solution of calcium bisulfite and agitated therewith to form normal calcium sulfite.

Where the solution of sodium sulfide and sodium carbonate is thus sulfited, the resulting cooking liquor will contain sodium sulfide and sodium sulfite, both of which are active chemicals in the cooking operation. For example, with a cooking liquor containing 20–25% of sodium sulfide on the air-dry weight of the wood the liquor may also contain 5 to 15% of sodium sulfite on the air-dry weight of the wood, although these amounts and the relative proportions of sulfide and sulfite are capable of variation.

The cooking liquor for the sulfide cooking process may also contain some caustic soda, although it is one advantage of the present invention that caustic soda may be entirely omitted, so that any causticizing operation in which lime is required and lime mud is produced may be eliminated. Where, however, caustic soda is desired in the process, it may be readily provided by causticizing some of the sodium carbonate with lime so as to form a cooking liquor containing mainly sodium sulfide, with varying amounts of caustic soda and either with or without other sodium compounds, such as sodium sulfite, sodium carbonate, etc.

The residual liquor from the sulfide cooking process is concentrated, for example, in evaporators and the concentrated liquor subjected to a drying and carbonizing or burn-

ing operation, preferably under oxidizing conditions in a current of hot gases which favor the removal of sulfur compounds during the calcination and facilitate the production of a recovered soda product which is free from or low in sodium sulfide, and which may advantageously contain some sodium sulfate. This operation can be carried out in a rotary calcining furnace, e. g. under oxidizing conditions, or by spraying the highly concentrated liquor into a hot furnace where it is burned under oxidizing conditions, whereby sulfur is largely oxidized and some of which may be removed, for example, as sulfur dioxide. The gases from such operation may be scrubbed to recover sulfur compounds therefrom, which may be returned to the cycle at a suitable point and made available in the process. For example, sulfur dioxide can be recovered from such gases and utilized for sulfiting sodium carbonate which is to be employed in the sulfite cooking liquor.

The solution of the furnace product in such case will contain the sodium compounds largely as sodium carbonate, with which varying amounts of other sodium salts may be present, such as sodium sulfate, sodium sulfide, etc. If the sodium sulfide content of the product is too high, it may be reduced, for example, by treating the solution with sufficient carbon dioxide to drive off hydrogen sulfide and thus increase the sodium carbonate content. When only small amounts of sodium sulfide are present they may remain in the solution when it is sulfited and may be to a greater or less extent converted into thiosulfate, although by sulfiting the solution hot, for example, with sodium bisulfite, and with agitation, the production of thiosulfate from sulfide can be prevented to a greater or less extent.

The solution of the furnace product containing mainly sodium carbonate is subjected to a sulfiting treatment. This treatment may be effected with sulfur dioxide, particularly where the sulfide content of the liquor is low. It may also be effected with a solution of sodium bisulfite or by means of calcium sulfite, produced, for example, as above described. As a result of the sulfiting treatment, a liquor is produced containing mainly sodium monosulfite with which varying smaller amounts of other sodium compounds may be present, such as sodium sulfide, sodium thiosulfate, sodium sulfate, etc.

The solution thus obtained can be used in the monosulfite cooking process, for example, utilizing upwards of 30% of monosulfite on the air-dry weight of the wood in the case of deciduous pulp woods and upwards of 35% for resinous pulp woods, and carrying out the cooking operation, for example, at a temperature of about 170–185° C. and at corresponding steam pressure for a sufficient time, with suitable circulation of the liquor and with thorough impregnation of the wood chips with the cooking liquor before the cooking liquor is heated to a high temperature during the cooking operation.

At the end of the cooking operation the pulp is separated from the residual liquor and such residual liquor can then be treated as herein described for the production therefrom of a sulfide cooking liquor.

The inter-related processes of the present invention can be employed with woods of various kinds, including both deciduous and coniferous woods, as described in our applications hereinbefore referred to.

Instead of utilizing all of the residual liquor from the respective processes for the production of cooking liquors for the other process, a part of the residual liquor from each process may be employed for other purposes, for example, for regenerating cooking liquor for the same process. For example, a larger number of digesters or cooks can be operated according to one process, than according to the other, only so much of the residual liquor from the major cooking operation as may be suitable being employed for producing the cooking liquor for the minor operation, the remainder of the cooking liquor from the major operation being employed for regenerating the cooking liquor for the same operation. Thus the residual liquor from the sulfite cooking process can be in part treated in the manner above described to produce a sulfide cooking liquor and the remainder can be treated for the regeneration of sulfite cooking liquor, for example, by adding such remainder to the residual sulfide liquor before it is treated in the manner above described to produce a sulfite cooking liquor. Similarly, some of the sulfide residual liquor can be utilized for the regeneration of additional sulfide cooking liquor, for example, by adding it to the sulfite residual liquor before it is treated in the manner above described for the production therefrom of sulfide cooking liquor. The process is thus elastic in character and capable of variation to adapt itself to mills of varying production by one or the other process. In mills where both cooking processes are utilized, different woods may be cooked by the different processes and different pulp products produced.

The sulfide cooking operation of the present invention is one in which the cooking liquor is advantageously free from polysulfide. If the reduction product or melt contains polysulfides these may be eliminated or reduced to the desired degree by treating the solution of the sodium salts to add sodium sulfite thereto or to form it therein, since this will react with polysulfide to form some thiosulfate. The presence of normal sulfite in excess of the amount theoretically required is advantageous, not only in modifying poly-

sulfides, but in modifying the cooking operation and the odors produced thereby, and the quality of the pulp produced.

When caustic soda is present in the liquor used in the sulfide cooking operation, the caustic as well as the sulfide will take part in the cooking operation and the sulfide can be reduced in amount as compared with the process when caustic soda is not present. Sodium sulfite supplements or increases the cooking power of the Na_2S.

The inter-related processes of the present invention will be further illustrated in a conventional and diagrammatic manner by the accompanying flow sheet.

In the flow-sheet digester No. 1 is a digester of the sulfide cooking process, in which the cooking liquor contains mainly sodium sulfide either without or with other ingredients, such as sodium carbonate, sodium sulfite, caustic soda, sodium thiosulfate, sodium sulfate, etc.

The digester charge is discharged to a blow-pit or separator, where the pulp is separated from the residual liquor and washed. The residual liquor and washings then pass to an evaporator such as a multiple effect evaporator, where a concentrated liquor is produced. This is supplied to a calcining furnace where the carbonizing and calcining takes place, preferably under oxidizing conditions with elimination of some sulfur as sulfur dioxide. The calcined product then passes to a dissolver, supplied with water or weak liquor and with sodium carbonate if necessary or desirable for make-up of sodium losses. The solution of sodium salts is then clarified and sulfited, for example, by adding a moderate amount of calcium sulfite to bring about clarification and a preliminary partial sulfiting of the liquor, separating the clarified liquor from the solids, and then by treating the clarified liquor in a sulfiting apparatus with a suitable amount of sulfur dioxide. The sulfited liquor can then be supplied to sulfite digester No. 2, where the sulfite cooking operation is carried out.

The sulfite cooking liquor may contain sodium sulfite alone or sodium sulfite together with preferably lesser amounts of sodium carbonate, sodium thiosulfate, sodium sulfide, caustic soda, sodium sulfate, or varying, preferably lesser amounts of two or more of these or other sodium salts.

The pulp and residual liquor after the cooking operation are discharged to a blow-put or other separating device where the residual liquor is removed, and the pulp washed, and the washings, together with the residual liquor, then passed to an evaporator, where a concentrated residual liquor is produced. This may then be fed into a calcining and reducing furnace, where the furnacing and reducing operation is carried out under conditions which will produce and retain a high sulfide content in the furnace product. Sodium sulfate for make-up may be added to the charge entering this furnace and the sodium sulfide content thereby increased and regulated.

The furnace product is then passed to a dissolving tank or apparatus where the soluble salts are dissolved in water or dilute liquor to give a solution containing mainly sodium sulfide and carbonate. This solution may then be sulfited, for example, with calcium sulfite, which treatment will also serve to clarify the solution, or a small amount of lime can be added to assist in clarification, or to produce the regulated amount of caustic soda in the liquor. In case calcium sulfite is used, the calcium carbonate produced is advantageously well washed to free it from sulfide if it is to be further treated with sulfur dioxide to regenerate additional calcium sulfite for reuse in a similar manner.

The regenerated liquor containing mainly sodium sulfide and sodium carbonate, or advantageously sodium sulfide and a smaller amount of sodium sulfite, etc., may then be supplied to the sulfide digester for use in carrying out the sulfide cooking operation.

In the flow sheet and description thus far given it is assumed that all of the residual liquor from one process is utilized in making cooking liquor for the other. Where, however, a larger amount of the cooking is to be carried out with one process than the other, an excess of one or the other residual liquors will be formed. This is provided for in the flow sheet by the dotted lines leading from the evaporator of one process to the calcining furnace of the other, whereby any suitable and desired amount of concentrated residual liquor from either process may be admixed with residual liquor from the other process and treated therewith in the manner above described.

It will thus be seen that the present invention provides an improved combination of inter-related processes in which the chemicals employed in each process, after they have served their purpose in that process, are treated for the production therefrom of chemicals for use in a cooking process of a different character. Furthermore, the processes and the chemicals used therein are so inter-related that advantage is taken of the high sulfur content of the sulfite residual liquors in producing a high sulfide content for the sulfide process; and advantage is also taken of the regeneration treatment to which the sulfide residual liquors are subjected to convert the sodium compounds into a form such that they can be advantageously treated for use in the sulfite process. In the treatment of the sulfite residual liquors it is desired to retain as much sulfur as feasible and to convert it into a reduced form such that it can be employed as sodium sul-

fide in the sulfide process; but in treating the residual liquors from the sulfide process, advantage is taken of the eliminating effect of the organic compounds present in the liquor to suitably alter or eliminate sufficient sulfur so that the resulting product is low in sulfide or may be free therefrom and can be readily and advantageously treated for the production of a suitable monosulfite cooking liquor. This characteristic sulfur eleminating action of the organic matter may be supplemented by oxidizing conditions which will assist in eliminating sulfur from the furnace product or which may convert it into an oxidized form such as sulfite or sulfate. Although sulfate may not be active in the sulfite cooking operation, nevertheless it remains and furnishes additional sodium sulfide when the residual liquor from the sulfite process is treated for the production of sulfide cooking liquor. When sodium thiosulfate is also present in the sulfite cooking liquor it may take part in the cooking operation and in addition it will supply additional sodium sulfide during the regenerative treatment of the sulfite residual liquor, thus facilitating the production of a high sodium sulfide content in this cooking liquor.

The sulfide cooking process, in addition to being an advantageous process for the production of pulp from wood, has the relation in the cyclic inter-related process of eliminating sulfur from sodium sulfide during the cooking and regenerative treatment, whereby the sodium of the sulfide can be recovered in an advantageous form well adapted for use in making cooking liquors for the sulfite process.

We claim:

1. The method of producing wood pulp from wood, which comprises cooking wood in a non-acid sodium monosulfite cooking liquor, cooking wood in a cooking liquor containing sodium sulfide as the main cooking constituent, and recovering sodium compounds from the residual liquor from each cooking operation and using the same in the formation of cooking liquor for the other cooking operation.

2. The method of producing wood pulp from wood, which comprises cooking wood in a non-acid sodium monosulfite cooking liquor, subjecting the residual liquor from such cooking operation to a concentrating, carbonizing and reducing treatment under conditions to produce a reduced product high in sodium sulfide, and cooking wood with a cooking liquor containing the sodium sulfide so produced as its main cooking ingredient.

3. The method of producing wood pulp from wood which comprises cooking wood with a non-acid cooking liquor containing sodium sulfide as its main ingredient, treating the residual liquor from such process by a concentrating and carbonizing treatment under conditions to eliminate sulfur and give a furnace product containing the sodium salts mainly as sodium carbonate and treating the resulting product to produce a monosulfite cooking liquor and cooking wood therewith.

4. The method of producing wood pulp from wood which comprises cooking wood in a non-acid sodium monosulfite cooking liquor, separating the residual liquor from the pulp and subjecting the residual liquor to evaporation and to calcination and reduction under conditions to give a furnace product containing a large amount of sodium sulfide, and forming from the furnace product a cooking liquor containing mainly sodium sulfide as the active cooking ingredient, cooking wood with such cooking liquor, separating such pulp from the residual liquor from such sulfide cooking operation, subjecting the residual liquor to concentration and to calcination under conditions to remove sulfur and give a furnace product containing the sodium compounds mainly as sodium carbonate forming a solution of the resulting sodium compounds and treating the same to produce a sulfite cooking liquor for the sulfite cooking process first mentioned, said treatment including a sulfiting treatment of the solution.

5. In the process of claim 4, the carrying out of the sulfiting operation so that sodium thiosulfate is produced in the sulfite cooking liquor and carrying out the sulfite cooking operation with the resulting composite cooking liquor containing mainly sodium sulfite and a smaller amount of sodium thiosulfate.

6. The method of producing wood pulp from wood, which comprises cooking wood in a non-acid sodium monosulfite cooking liquor, subjecting the residual liquor from such cooking operation to a concentrating, carbonizing and reducing treatment under conditions to produce a reduced product high in sodium sulfide, forming a solution of soluble sodium salts consisting mainly of sodium sulfide and sodium carbonate, treating such solution with a reactive calcium compound to form calcium carbonate and convert part of the sodium carbonate into an active sodium compound, and cooking wood with the resulting solution as a cooking liquor.

7. The method of producing wood pulp from wood, which comprises cooking wood in a non-acid sodium monosulfite cooking liquor, subjecting the residual liquor from such cooking operation to a concentrating, carbonizing and reducing treatment under conditions to produce a reduced product high in sodium sulfide, forming a solution of soluble sodium salts consisting mainly of sodium sulfide and sodium carbonate, treating the solution with calcium sulfite to convert sodium carbonate into sodium sulfite and forming insoluble

calcium carbonate, and cooking wood with the resulting cooking liquor containing sodium sulfide and sodium sulfite.

8. The method of producing wood pulp from wood, which comprises cooking wood in a non-acid sodium monosulfite cooking liquor, subjecting the residual liquor from such cooking operation to a concentrating, carbonizing and reducing treatment under conditions to produce a reduced product high in sodium sulfide, forming a solution of soluble sodium salts consisting mainly of sodium sulfide and sodium carbonate, treating the solution with lime to convert sodium carbonate into sodium hydroxide and cooking wood with the resulting cooking liquor containing sodium sulfide and sodium hydroxide.

9. The method of producing wood pulp from wood, which comprises cooking wood in a non-acid sodium monosulfite cooking liquor, subjecting the residual liquor from such cooking operation to a concentrating, carbonizing and reducing treatment under conditions to produce a reduced product high in sodium sulfide, forming a solution of soluble sodium salts consisting mainly of sodium sulfide and sodium carbonate, treating the solution with calcium sulfite and calcium hydroxide to convert sodium carbonate into sodium sulfite and sodium hydroxide, and cooking wood with the resulting cooking liquor containing sodium sulfide, sodium sulfite and sodium hydroxide.

10. The method of producing wood pulp from wood, which comprises cooking wood in a non-acid sodium monosulfite cooking liquor, subjecting the residual liquor from such cooking operation to a concentrating, carbonizing and reducing treatment under conditions to produce a reduced product high in sodium sulfide, forming a solution of soluble sodium salts consisting mainly of sodium sulfide and sodium carbonate, treating the solution with lime to convert sodium carbonate into sodium hydroxide and cooking wood with the resulting cooking liquor containing sodium sulfide and sodium hydroxide, the amount of sodium carbonate converted into sodium hydroxide being such that the cooking liquor contains a greater amount of sodium as sodium sulfide than as caustic soda.

In testimony whereof we affix our signatures.

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