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PRODUCTION OF CHEMICAL PULP

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This invention relates to the production of chemical pulp, and to the treatment of residual liquors for the regeneration of cooking liquors.

More particularly the invention relates to cyclic and interrelated operations in which two different kinds or types of sulfur-containing liquors are employed in cooking operations, of which soda is the base, some of the same sulfur being present as sodium sulfite in one type of cooking liquor, in one instance, and being present as sodium sulfid in one of the cooking liquors, in another instance, and with successive employment of some of the same soda as sodium sulfite and, in a succeeding operation, as sodium sulfid, although the soda and the sulfur may in part be present as other compounds.

Among the particular improvements which the invention presents are interrelated operations or steps in which cooking liquor for one type of cooking operation is regenerated (at least in part) from residual liquor constituents from another type of cooking operation. The two kinds or types of cooking liquors, to which the invention more particularly relates, are those which may be described in the following general manner. One contains as much and usually more sodium hydroxide than sodium sulfid and is generally free from any large amount of sodium sulfite; the other generally contains as much, and usually more, of its soda content in the form of sodium sulfite as is present therein in the form of sodium sulfid, and either contains a lesser amount of sodium hydroxide than of sodium sulfid or is free from sodium hydroxide. The cooking liquor first described is called the caustic cooking liquor, owing to its high content of NaOH; the other cooking liquor is called the sulfid cooking liquor, owing to the cooking being primarily due to its content of Na_2S.

According to one embodiment of the invention, one lot of wood chips is cooked in a suitable amount of the caustic cooking liquor, thereby producing chemical pulp and a residual liquor, another lot of wood is cooked in a suitable amount of the sulfid cooking liquor, thereby producing chemical pulp and a residual liquor different in type as compared with the other residual liquor, the pulps are separated from the residual liquors, respectively, and residual liquor from one cooking operation is admixed with residual liquor from the other cooking operation, the admixed liquor is concentrated and the product subjected to a furnacing treatment under reducing conditions, thereby decomposing organic compounds and forming a product which contains mainly sodium carbonate and a relatively high content of sodium sulfid. The furnacing operation, which may be carried out after previously subjecting the concentrated mixture of residual liquors to treatment by gases from the furnace which contain sulfur compounds, is advantageously so regulated that the resulting soda product contains a considerable portion of the sulfur content of the admixed residual liquors in the form of sodium sulfid, care being taken to avoid driving off an excessive amount of such sulfur along with the gases. Any combustible sulfur compounds carried by the gases may be subjected to an oxidizing treatment, e. g. by admixing a regulated amount of air therewith, and some of such oxidized sulfur compounds may be absorbed in the residual liquor which is subjected to the action of such gases. By employing such liquor in a disc-evaporator, some of such sulfur may be regained from the furnace gases which are caused to pass through it.

The soda compounds produced as a result of such treatment, are dissolved in water to form a suitable solution. A regulated portion of such solution is causticized with suf-

ficient lime to form a cooking liquor of the caustic type, and another portion thereof is sulfited to form the required amount of sodium sulfite for the sulfid cooking liquor. Such sulfiting step may be carried out in any suitable manner. For example, one portion may be subjected to a direct sulfiting treatment, provided the solution contains a suitable ratio of sodium carbonate to sodium sulfid, and for this purpose some sodium carbonate may be dissolved in such portion of the solution which is to be so sulfited. Such sodium carbonate may be that which is added for replenishing the soda required for the cycle. The sodium sulfite solution thus prepared may be admixed with the required amount of untreated solution, so as to form a cooking liquor which contains the required amount of sodium sulfid and of sodium sulfite. The cooking liquor thus prepared will usually contain sodium thiosulfate. Another method of sulfiting the sodium carbonate in a portion of the solution of sodium carbonate and sodium sulfid, comprises adding thereto the required amount of calcium monosulfite, preferably freshly prepared, agitating the mixture long enough to form the desired amount of sodium sulfite in the liquor with a corresponding amount of calcium carbonate, after which the solution may be separated from the solids in any suitable manner. Such cooking liquor may contain little if any sodium thiosulfate, being composed primarily of sodium sulfid and sodium sulfite and accompanied by such an amount of sodium carbonate as remains unchanged. The caustic cooking liquor, and the sulfid cooking liquor, which have been regenerated in the manner described, are employed in their respective type of cooking operation.

Where sodium sulfate is added to the cycle for replenishing the soda, it is preferably added to the product which is to be subjected to the reducing furnace treatment, thereby augmenting or supplementing the sodium-sulfur constituents and thus facilitating the production of a soda product which contains a sufficiently high content of sodium sulfid. Sodium sulfid may be added for replenishing soda and may be added to cooking liquor of either type and advantage taken of such addition to form cooking liquor which contains the desired content of sodium sulfid as compared with the other constituents thereof. Sodium hydroxide, if employed for replenishing soda, is usually added to the caustic cooking liquor after it is separated from the lime mud resulting from the causticizing treatment.

The following examples will serve to illustrate the two types of cooking liquors, the amount of reagents being expressed in pounds and being based on a charge of 4,000 pounds of wood (oven-dry basis) such as poplar. For woods which require more chemical than does poplar, the amounts may be varied to suit the conditions.

Caustic cooking liquors

$NaOH$	Na_2S	Na_2SO_3	Na_2CO_3
600	200		200
500	300		150
400	350	300	200
500	250	300	200
400	350		400

Sulfid cooking liquors

Na_2S	Na_2SO_3	Na_2CO_3	$NaOH$
600	1280	300	
600	640	250	100
560	1000	300	
450	800	300	350
600	1100	250	100
560	1900	300	

Some sodium sulfate, or/and some sodium thiosulfate may be present in such cooking liquors or any of them, but these are usually present in only moderate amount, if at all.

The cooking operations of the present invention may be carried out either in a single stage or in a multiple stage. For example enough cooking liquor, containing the required amount of active chemicals, may be charged into a digester containing the freshly charged chips and the contents subjected to a suitable elevated temperature until the cooking operation has reached a point whereby good chemical pulp may be produced by blowing the contents of the digester into a blow-pit in the usual way. Alternatively, the freshly charged chips may be given a preliminary treating operation to remove some of the more readily removable constituents thereof, and the final pulping treatment be carried out thereafter by introducing sufficient cooking liquor of suitable composition into the digester which contains the partially treated chips and thereafter concluding the pulp-producing operation. The residual liquor separated from the pulp after completion of the pulping operation, may be employed to effect the preliminary treatment of the freshly charged chips, and such residual liquor may be employed without modifying it or it may have active reagents added thereto to fortify it and thus to increase its activity, such as NaOH, or/and Na_2S. Thus the composition of the liquor employed in the stages may differ considerably. In the concluding stage, the cooking liquor either contains both sodium hydroxide and sodium sulfid in regulated amounts, or sodium sulfid and sodium sulfite, thus securing the combined advantages of such reagents in the final stage of the cooking operation. When the two-stage method of cooking is employed, it appears to be possible to produce good quality pulp from wood by employing a smaller amount of active chemicals than where the entire pulping operation is carried

from the digestion of cellulosic material in an alkaline cooking liquor containing caustic soda as its main constituent, thereby producing a furnace product containing its sodium compounds mainly in the form of sodium carbonate and sodium sulfid, and treating such sodium compounds to produce an alkaline cooking liquor for the alkaline cooking liquor for the alkaline digestion of cellulosic material.

4. The process which comprises subjecting to a furnacing treatment under reducing conditions the inorganic content with admixed organic matter of a concentrated mixture of the waste residual liquor resulting from the digestion of cellulosic material in a solution of sodium-sulfur salts containing most of the sodium in the form of a sulfite of sodium and the residual liquor resulting from the digestion of cellulosic material in an alkaline solution containing sodium compounds, the major portion of which are sulfur-free sodium compounds, thereby producing a furnace product containing the sodium compounds mainly as sodium carbonate and sodium sulfid, and treating the resulting sodium compounds to produce an alkaline cooking liquor for the digestion of cellulosic material, the gaseous products from the reducing furnacing treatment being passed into contact with residual liquor for the recovery of inorganic constituents therefrom in the liquor before the inorganic constituents of such liquor are subjected to the reducing furnacing treatment.

5. The process which comprises subjecting to a furnacing treatment under reducing conditions the inorganic content with admixed organic matter of a concentrated mixture of the waste residual liquor resulting from the digestion of cellulosic material in a solution of sodium-sulfur salts containing most of the sodium in the form of a sulfite of sodium and the residual liquor resulting from the digestion of cellulosic material in an alkaline solution containing sodium compounds, the major portion of which are sulfur-free sodium compounds, thereby producing a furnace product containing the sodium compounds mainly as sodium carbonate and sodium sulfid, and treating the resulting sodium compounds to produce cooking liquors of the types employed in the respective digestion treatments.

6. The process which comprises subjecting to a furnacing treatment under reducing conditions the inorganic content and admixed organic matter of a concentrated mixture of two different kinds of residual liquors resulting from the digestion of cellulosic material, one of said residual liquors resulting from digestion of cellulosic material in cooking liquor containing a sulfite of sodium as its main constituent, and the other residual liquor resulting from digestion of cellulosic material in a cooking liquor containing caustic soda and sodium sulfid as its main constituents, thereby producing a furnace product containing its sodium compounds mainly in the form of sodium carbonate and sodium sulfid, and treating the resulting sodium compounds to produce cooking liquors of the types employed in the respective digestion treatments.

7. The process which comprises subjecting to a furnacing treatment under reducing conditions the inorganic content and admixed organic matter of a concentrated mixture of residual liquors resulting from the digestion of cellulosic material, one of said residual liquors resulting from the digestion of cellulosic material in an alkaline solution of sodium sulfite containing the greater part of its sodium in the form of sodium sulfite, and the other of said residual liquors resulting from the digestion of cellulosic material in an alkaline cooking liquor containing caustic soda as its main constituent, thereby producing a furnace product containing its sodium compounds mainly in the form of sodium carbonate and sodium sulfid, and treating the resulting sodium compounds to produce cooking liquors of the types employed in the respective digestion treatments.

8. The process which comprises subjecting to a furnacing treatment under reducing conditions the inorganic content and admixed organic matter of residual liquor resulting from the digestion of cellulosic material in a cooking solution of sodium-sulfur salts and containing a sulfite of sodium as the main sodium salt, and thereby producing a furnace product containing its sodium compounds mainly in the form of sodium carbonate and sodium sulfid, and treating the resulting furnace product to form a cooking liquor containing the sodium sulfid of such furnace product as one of its main constituents and digestion cellulosic material therewith.

In testimony whereof we affix our signatures.

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out in one stage and the reactive constituents of the freshly charged cooking liquor are the same, e. g. where sodium sulfid and sodium sulfite are the active constituents of the freshly charged liquor. By subjecting the freshly charged chips to a treatment at elevated temperature with a liquor, which may either be a fortified or an unfortified residual liquor, or a freshly charged liquor containing little or no organic matter, so that about one half of the non-cellulose material is removed from the digester, e. g. in solution or/and in suspension therein, about two thirds of the amount of active chemical ordinarily employed in a single stage cook, may be sufficient when employed in the cooking liquor for completing the pulping operation. The liquor employed in the preliminary treatment may even be a solution of sodium carbonate and sodium sulfid which has not been causticized or sulfited, such liquor being able to remove quite a large amount of non-cellulose material from the wood and leaving the chips in better condition for the final pulping treatment than if they had not been so treated. Thus a part only of the sodium carbonate-sodium sulfid solution may be sulfited, e. g. by $CaSO_3$, to form a cooking liquor for the second stage treatment which contains primarily sodium sulfite and sodium sulfid and such liquor being employed in the final pulping stage, the chips having been previously treated by residual liquor or by sodium carbonate-sodium sulfid liquor so as to remove a considerable amount of non-cellulose material therefrom, e. g. so that about one fourth to one half of the non-cellulose is thus removed in the preliminary treatment. The residual liquor from the caustic cooking treatment of wood may be advantageously employed for such preliminary treatment of the lot of chips which is to be further treated by Na_2S, etc. Such utilization of the residual liquor from a caustic cooking operation is advantageously carried out prior to admixing such residual liquor with that which results from the utilization of sodium sulfid and sodium sulfite for the treatment of freshly charged wood or for the final pulping treatment of wood which has been partially treated. After removal of the residual liquors from the wood or from the pulp, they are admixed and thereafter concentrated. Some of the residual liquor of the cycle may be concentrated without admixing it with other residual liquor, and such product may be subjected to a separate furnace treatment to produce a recovered soda product. Such furnace treatment may be carried out in any suitable manner and the soda utilized or disposed of as desired.

The steps of the cycle described in this specification facilitate the production of a recovered soda product which contains a considerable amount of sodium sulfid, and, especially when the soda losses are kept down to a low point, the sulfur utilization disclosed is taken advantage of for the production, on the one hand, of caustic cooking liquors which contain a desirable ratio of NaOH to Na_2S; and the operation may be regulated to this end. Various woods may be pulped by the cooking liquors described, and various pulps thereby produced.

This application is in part a continuation of our applications Serial Nos. 456,187, filed March 28, 1921; 481,146 and 481,147, filed June 28, 1921; 686,137, filed Jan. 14, 1924; and 757,766, filed Dec. 23, 1924.

We claim:

1. The process which comprises subjecting to a furnacing treatment under reducing conditions the inorganic content with admixed organic matter of a concentrated mixture of the waste residual liquor resulting from the digestion of cellulosic material in a solution of sodium-sulfur salts containing most of the sodium in the form of a sulfite of sodium and the residual liquor resulting from the digestion of cellulosic material in an alkaline solution containing sodium compounds the major portion of which are sulfur-free sodium compounds, thereby producing a furnace product containing the sodium compounds mainly as sodium carbonate and sodium sulfid, and treating the resulting sodium compounds to produce an alkaline cooking liquor for the digestion of cellulosic material.

2. The process which comprises subjecting to a furnacing treatment under reducing conditions the inorganic content and admixed organic matter of a concentrated mixture of two different kinds of residual liquors resulting from the digestion of cellulosic material, one of said residual liquors resulting from digestion of cellulosic material in cooking liquor containing a sulfite of sodium as its main constituent, and the other residual liquor resulting from digestion of cellulosic material in a cooking liquor containing caustic soda and sodium sulfid as its main constituent, thereby producing a furnace product containing its solution compounds mainly in the form of sodium carbonate and sodium sulfid, and treating such sodium compounds to produce an alkaline cooking liquor for the alkaline digestion of cellulosic material.

3. The process which comprises subjecting to a furnacing treatment under reducing conditions the inorganic content and admixed organic matter of a concentrated mixture of residual liquors resulting from the digestion of cellulosic material, one of said residual liquors resulting from the digestion of cellulosic material in an alkaline solution of sodium sulfite containing the greater part of its sodium in the form of sodium sulfite, and the other of said residual liquors resulting

CERTIFICATE OF CORRECTION.

Patent No. 1,797,678. Granted March 24, 1931, to

LINN BRADLEY ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, line 113, claim 2, for the word "constituent" read constituents, and line 114, for "solution" read sodium; page 4, lines 8 and 9, claim 3, beginning with the word "cooking" second occurrence, strike out the words "cooking liquor for the alkaline"; same page, line 107, claim 8, for "digestion" read digesting; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 28th day of April, A. D. 1931.

M. J. Moore,
Acting Commissioner of Patents.

(Seal)