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PRODUCTION OF PULP, ETC.

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This invention relates to the production of chemical pulp from wood and to the regeneration of the cooking liquors.

More particularly it relates to the cooking of wood chips with cooking liquors which contain sodium sulfide and sodium sulfite as the primary or the sole active reagents, and to the treatment of the residual liquors therefrom and the regeneration of cooking liquors for use in the same type of cooking process. Moderate amounts of other chemicals may be present in the cooking liquors, e. g. sodium hydroxide, sodium carbonate, sodium thiosulphate, sodium sulphate.

Among the objects of the invention is the control of the various steps whereby the operation may be cyclic in character, especially when the cooking liquor contains a relatively large amount of sodium sulphide as compared with sodium hydroxide. Other objects will appear from the following more detailed description.

According to this invention, wood chips are digested in cooking liquor which contains a considerable amount of sodium sulfide as an active reagent, the amount of sodium sulfide being equal to or advantageously greater than the amount of sodium hydroxide, and containing a substantial amount of sodium sulfite; the residual liquor, referred to herein as black liquor, is separated from the pulp, the pulp is washed and the washings (a suitable amount) is added to the black liquor (the mixture being referred to as weak black liquor); the weak black liquor is concentrated, the organic matter is decomposed by heat treatment, the sodium compounds being obtained principally in the form of sodium sulfide and sodium carbonate. A solution of suitable strength is prepared from the recovered sodium carbonate and sodium sulfide, and a cooking liquor is prepared therefrom which is thereafter utilized in the digesting step.

In the preferred embodiment of the invention, the cooking liquor is either substantially free from sodium hydroxide, or the sodium hydroxide is present in limited amount, e. g. less than the amount of sodium sulfide. For examples: the cooking liquor may contain 50 parts as Na_2S, 25 parts as NaOH, 25 parts as Na_2SO_3, all being computed on an Na_2O basis; that is to say, about 50 parts Na_2S, about 25.64 parts NaOH, and about 40.39 parts Na_2SO_3.

50 parts as Na_2S, 40 parts as Na_2SO_3, 10 parts as NaOH; that is to say, about 50 parts of Na_2S, 64.62 parts Na_2SO_3, 10.26 parts NaOH.

50 parts as Na_2S, 45 parts as Na_2SO_3, 5 parts as NaOH; that is to say, about 50 parts of Na_2S, 72.7 parts of Na_2SO_3, 5.13 parts of NaOH.

Various other ratios of these active compounds may be contained in the cooking liquors of this process, and other chemicals may be present in moderate amounts, e. g. Na_2CO_3, $Na_2S_2O_3$, Na_2SO_4, etc. The amount of the active reagents used, in proportion to the wood digested by such cooking liquors may vary somewhat, but sufficient sodium sulphide is employed to perform a very substantial portion of the digestion, which may be supplemented by the NaOH and the Na_2SO_3, or by the Na_2SO_3 alone when no NaOH is present.

In computing the activity of the cooking liquor, all of the NaOH and of the Na_2S is considered as available, and from ¼ to ½ of the Na_2SO_3 is likewise considered. Some of the Na_2SO_3 appears to be converted into $Na_2S_2O_3$ in the digestion step as a result of the reaction between Na_2S and wood substance. An activity of about 18 to 25% (Na_2S equivalent) is generally sufficient for most woods, the higher amounts being employed for wood which requires more chemicals to yield the desired product from the wood.

The digestion or cooking step is carried

out in a manner similar to that employed in the usual soda process or the so-called sulphate process, as to time, temperature, pressure, etc., but the cooking operation will be modified owing to the difference in the cooking liquor employed.

The sodium sulphite present in the liquor appears to reduce the amount of sulphur which escapes with the vapors when the digester is relieved and when the digester contents are blown at the end of the cook. This appears to modify the odors in an advantageous manner, and is further desirable owing to the retention of the sulphur in the residual liquor.

When the residual liquor is concentrated and the organic matter is decomposed by heat treatment in the presence of a current of hot gases, some sulphur is eliminated along with the gases. In order to retain a considerable amount of sulphur in the product, the furnacing operation is so carried out as to facilitate the production of sodium sulfide in the recovered soda product. For example, the stack gases are scrubbed by the black liquor so as to absorb some of the soluble sulphur compounds and to regain some of the soda carried by the gases. Air is introduced at any suitable point, e. g. between the calcining furnace and the scrubber so as to oxidize some sulphur compounds, e. g. H_2S, COS, etc. if present, so as to facilitate their recovery by the scrubbing operation and thus promote the production of a recovered product containing a high percentage of Na_2S. The hot furnace gases appear to eliminate some of the sulphur as COS by interaction between CO_2 and S. When the COS is burned some SO_2 or SO_3 is formed which is more easily absorbed in the black liquor used in the scrubber. The furnace operation is so conducted as to obtained a high percentage of Na_2S and care is taken not to prolong the furnace operation.

The sodium carbonate and sodium sulphide and other soluble sodium compounds in the recovered furnace product are dissolved in water or weak cooking liquor, for example, and the solution is clarified by any suitable means before being employed in the cooking operation.

Sodium sulphate may be employed for replacing soda losses which are, however, kept low owing to the scrubbing of the stack gases. Sodium sulphate may be added at any suitable point, e. g. to the material entering the furnace in which the reduction treatment occurs by which Na_2S is formed.

In case some NaOH is desired in the cooking liquor, a suitable amount of $Ca(OH)_2$ may be added to the Na_2CO_3-Na_2S liquor to convert the desired portion of Na_2CO_3 into NaOH. The $CaCO_3$ mud formed aids in the clarification of the liquor. By keeping the amount of NaOH thus produced and the amount of lime mud thus formed, down to a very low point, there is an advantage owing to the lesser amount of lime mud to be washed in order to regain the soda. Where no lime is used, and no NaOH is thus formed, the washing of such lime mud is dispensed with, which is a distinct advantage.

In case Na_2SO_3 is desired in the cooking liquor, in greater amount than already present in the Na_2S-Na_2CO_3 liquor, a further amount of Na_2SO_3 may be formed therein by treating the solution with the required amount of $CaSO_3$. The mixture is agitated for sufficient time to convert the $CaSO_3$ for the most part or substantially completely, into $CaCO_3$ and form a corresponding amount of Na_2SO_3 in the solution by reaction with Na_2CO_3 thereof. The liquor is separated from the $CaCO_3$ mud, the latter is washed to remove the soda compounds to a considerable extent, thus freeing the $CaCO_3$ mud from most of the sulphide associated therewith in the solution. After such washing, the $CaCO_3$ mud may then be more advantageously treated with an acid sulphite solution, e. g. a solution prepared by dissolving SO_2 in water. This treatment is so regulated that substantially all of the $CaCO_3$ is converted into $CaSO_3$. The mixture of the acid solution and the $CaCO_3$ is suitably agitated to promote the reaction, and when substantially all of the $CaCO_3$ has been thus converted, and that solution has been nearly or substantially neutralized by removal of uncombined SO_2, the mud is separated from the liquor. This mud may be used for converting more Na_2CO_3 into Na_2SO_3 in the manner above outlined.

The liquor may be used for absorbing more SO_2 to prepare another charge of acid sulphite solution to be employed for treating another batch of $CaCO_3$ mud. It is advantageous to thus reuse the liquor owing to the retention of the soda compounds which may be present therein, e. g. when the $CaCO_3$ mud has not been fully washed to remove the soda compounds. Too much Na_2S should not be permitted to remain in the $CaCO_3$ mud since this is readily converted into some $Na_2S_2O_3$ when treated with the acid sulphite solution. A small amount of Na_2S may be thus tolerated and simplification of the washing problem effected.

Some Na_2CO_3 may be added to the cycle at any suitable point, e. g. it may be dissolved in the solution which is to be sulfited. In this case the free or uncombined SO_2 is still relied upon for treating the $CaCO_3$. Any sodium sulphite remaining in the solution accompanying the $CaSO_3$ may be transferred to the cooking liquor, i. e. when the $CaCO_3$ mud is washed to remove cooking liquor. Thus the strength of the circulating sulphite solution, and the amount of liquor carried along by the $CaSO_3$ mud, may be regulated

so as to introduce the desired portion of soda as Na_2SO_3. By using a dilute circulating sulphite solution, and removing most of the solution from the $CaSO_3$ mud, the amount of soda thus removed may be kept very low, and still have it present in the solution.

When the $CaSO_3$ mud or the $CaCO_2$ mud becomes fouled, from any cause, the whole or any required portion thereof may be discarded, preferably as $CaCO_3$ mud. This should be well washed before it is discharged, to regain the soda. If desired the $CaCO_3$ mud, or a portion thereof, which is to be discarded, may be employed, prior to its being discarded, for the treatment of the $NaCO_3$-Na_2S liquor to clarify it. The mud and sediment, e. g. carbon, etc., may be washed and the washings retained and the washed mud discarded.

The make-up of lime compounds may be supplied in any suitable manner, e. g. it may be advantageously supplied by adding CaO, or $Ca(OH)_2$ in the required amount to replace losses, to the liquor which contains the Na_2CO_3-Na_2S to form a corresponding amount of NaOH therein. The $Ca(OH)_2$ may even be mixed with the $CaSO_3$ mud and the two employed together or the make-up lime may be added in part to the Na_2CO_3-Na_2S liquor to clarify it and another portion of $Ca(OH)_2$ to the $CaCO_3$ or the $CaSO_3$ which is first sulphited and then used to produce Na_2SO_3 and is returned to be again sulphited. By first clarifying the liquor, and freeing it from any objectionable compounds, e. g. iron compounds, and avoiding objectionable compounds in the $CaCO_3$ mud or the $CaSO_3$ mud, these muds may be utilized over and over again for several times, thus minimizing the problem of discarding a portion thereof in order to remove accumulated objectionable material.

The amount of sulphur burned to form SO_2 and then, indirectly form Na_2SO_3 by the means described, can be regulated. Ordinarily the amount will be regulated so that the desired Na_2S content may be obtained in the cooking liquor. Where the sulphur retention is very high, e. g. owing to good scrubber recovery, the amount of SO_2 sulphur thus supplied can be kept very low, and especially where Na_2SO_4 is added for make-up.

The amount of SO_2 added to the cycle should be enough to insure the production of the required amount of Na_2S in the cooking liquor, and where the amount of NaOH in the cooking liquor is very low, such a high sulphide is desirable as will carry out most of the cooking operation, being supplemented by the moderate amount of Na_2SO_3 present. When the cooking liquor is free from or very low in NaOH, the Na_2SO_3 produced should be somewhat more than sufficient to convert polysulphides, if present, into normal sulphide and into some $Na_2S_2O_3$. Care should be taken, however, in the furnacing operations, to keep the polysulphides down to a very low point, and preferably absent from the Na_2S-Na_2CO_3 liquor. By having a considerable amount of Na_2SO_3 in the cooking liquor, a high Na_2S content may be safely employed and obtain high quality pulp. The Na_2SO_3 appears to overcome several objections to the use of a high Na_2S alone.

By this process, a large number of woods may be readily converted into chemical pulp of high quality and high yield. The process is cyclic in character, and the soda content can be repeatedly used in the manner outlined.

The present case is a continuation in part of our co-pending applications Serial Nos. 57,953 and 57,954, filed September 22, 1925.

We claim:

1. The method of producing wood pulp from wood which comprises cooking the wood in a cooking liquor comprising as its three essential chemical reagents sodium hydroxide, sodium sulfid and sodium sulfite, the sodium oxide equivalent of the sulfid being greater in amount than the Na_2O content of either the sodium hydroxide or the sodium sulfite, and the amount of sodium present as sodium sulfite being at least one half but less than the amount of sodium present as sodium sulfid.

2. The process which comprises cooking raw cellulosic material in an alkaline cooking liquor containing as essential chemical reagents sodium sulfid and sodium sulfite, separating the pulp from the spent cooking liquor, concentrating the spent liquor and calcining the dried product under reducing conditions to produce a furnace product containing sodium sulfid and sodium carbonate with evolution of sulfur-bearing gases from the furnace during the furnacing operation, oxidizing the gases from the furnacing operation with air and passing the oxidized gases in contact with spent cooking liquor for the recovery of oxidized sulfur compounds from the gases in the spent liquor, removing water from the resulting spent liquor, furnacing the resulting dried product under reducing conditions to form sodium carbonate and sodium sulfid, preparing a solution containing such sodium carbonate and sodium sulfid, sulfiting sodium carbonate thereof to prepare cooking liquor containing the sodium sulfid and sodium sulfite, and cooking raw cellulosic material with the prepared cooking liquor.

3. The further improvement in claim 2 in which the alkaline cooking liquor contains sodium present as sodium sulfite in an amount not less than one half but less than that present in the sodium sulfid.

4. The further improvement in claim 2, in which the alkaline cooking liquor contains

sodium sulfid, sodium sulfite and sodium hydroxide as its three essential chemical ingredients, such liquor containing more sodium present as sodium sulfid than as sodium hydroxide and the amount of sodium present therein as sodium sulfite being not less than one half but less than the amount of sodium present as sodium sulfid.

5. The method of producing pulp from wood, which comprises digesting the wood in an alkaline cooking liquor containing as its essential chemical reagents sodium sulfid and sodium sulfite, the amount of sodium present therein as sodium sulfite being not less than one half but less than the amount of sodium present therein as sodium sulfid and said liquor being free from sodium hydroxide in amounts larger than one half the amount of sodium sulfid therein.

6. The method of producing pulp from wood, which comprises digesting the wood in an alkaline cooking liquor containing as its three essential chemical reagents sodium sulfid, sodium sulfite and sodium hydroxide, the liquor containing for each 50 parts of sodium sulfid at least 25 parts but not more than 45 parts of sodium sulfite and at least 5 parts but not more than 25 parts of sodium hydroxide, all being computed on an Na_2O basis.

7. The process which comprises the following steps:—(*a*) digesting raw cellulosic fibre-bearing material in an alkaline cooking liquor containing sodium sulfid and sodium sulfite; (*b*) separating the resulting alkaline liquor from the resulting fibre-bearing material; (*c*) removing water from the resulting alkaline liquor; (*d*) furnacing dried constituents thereof under reducing conditions to form sodium carbonate and sodium sulfid; (*e*) dissolving these latter sodium compounds in water, thereby forming an alkaline solution; (*f*) treating the alkaline solution with material including a normal sulfite of an alkaline earth metal to convert sodium carbonate thereof into sodium sulfite, thereby producing an alkaline cooking liquor which contains sodium sulfid and sodium sulfite; (*g*) separating the alkaline cooking liquor from the resulting alkaline earth metal carbonate; (*h*) digesting raw cellulosic fibre-bearing material with the alkaline cooking liquor; (*i*) converting the alkaline earth metal carbonate into an alkaline earth metal sulfite by means of available SO_2; (*j*) and using such metal sulfite to treat an alkaline solution which contains sodium carbonate and sodium sulfid obtained as a result of the furnacing of dried constituents as per step (*d*).

8. The cyclic process which comprises the following steps:—(*a*) digesting raw cellulosic fibre-bearing material in a cooking liquor containing a sulfite of sodium; (*b*) separating the resulting liquor from the resulting fibre-bearing material; (*c*) removing water from the resulting liquor; (*d*) furnacing dried constituents thereof under reducing conditions to form sodium carbonate and sodium sulfid; (*e*) dissolving these latter sodium compounds in water, thereby forming an alkaline solution; (*f*) treating the alkaline solution with material including calcium hydroxide to convert a portion only of the sodium carbonate thereof into sodium hydroxide; (*g*) separating the partly causticized solution from the resulting calcium carbonate, thereby effecting a clarification of the solution; (*h*) sulfiting the clarified liquor to convert sodium carbonate thereof into sodium sulfite; (*i*) and digesting raw cellulosic-fibre-bearing material with cooking liquor containing the resulting sodium compounds.

9. The cyclic process which comprises the following steps:—(*a*) digesting raw cellulosic fibre-bearing material in a cooking liquor containing sodium sulfid and sodium sulfite; (*b*) separating the resulting liquor from the resulting fibre-bearing material; (*c*) removing water from the resulting liquor; (*d*) furnacing dried constituents thereof under reducing conditions to form sodium carbonate and sodium sulfid; (*e*) dissolving these latter sodium compounds in water, thereby forming an alkaline solution; (*f*) treating the alkaline solution with material including calcium hydroxide to convert a portion only of the sodium carbonate thereof into sodium hydroxide; (*g*) separating the partly causticized solution from the resulting calcium carbonate, thereby effecting a clarification of the solution; (*h*) treating the clarified solution with a sulfite of an alkaline earth metal to convert sodium carbonate thereof into sodium sulfite and produce an alkaline cooking liquor containing sodium sulfid and sodium sulfite; (*i*) separating the alkaline cooking liquor from the resulting carbonate of the alkaline earth metal; (*j*) and digesting raw cellulosic fibre-bearing material in such alkaline cooking liquor.

10. The further improvement in the process of claim 9, characterized by sulfiting the carbonate of alkaline earth metal with available SO_2, after it has been separated from the alkaline cooking liquor in step (*i*) thereof, and subsequently using the resulting sulfite of alkaline earth metal in step (*h*) thereof.

11. In a cyclic process for producing pulp from wood in which wood is digested by means of cooking liquor that contains at least as much of sodium sulfid as of sodium hydroxide and in which the residual liquor is evaporated and the sodium compounds thereof are subjected to a reducing furnace treatment to provide sodium carbonate and sodium sulfid and some of the sodium carbonate is converted into sodium hydroxide by means of lime, the improvement which comprises supplying sulfur to the cooking liquor of the

cycle in the form of the sulfite radical in such an amount that the cooking liquor contains at least one half as much but not more sodium as sodium sulfite as it contains as sodium sulfid, thereby providing the cooking liquor with sodium sulfite in amount sufficient to modify objectionable odors of the conventional sulfate process and providing the residual liquor with oxy-sulfur material sufficient to insure the presence of sodium sulfid in the regenerated cooking liquor.

In testimony whereof we affix our signatures.

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