

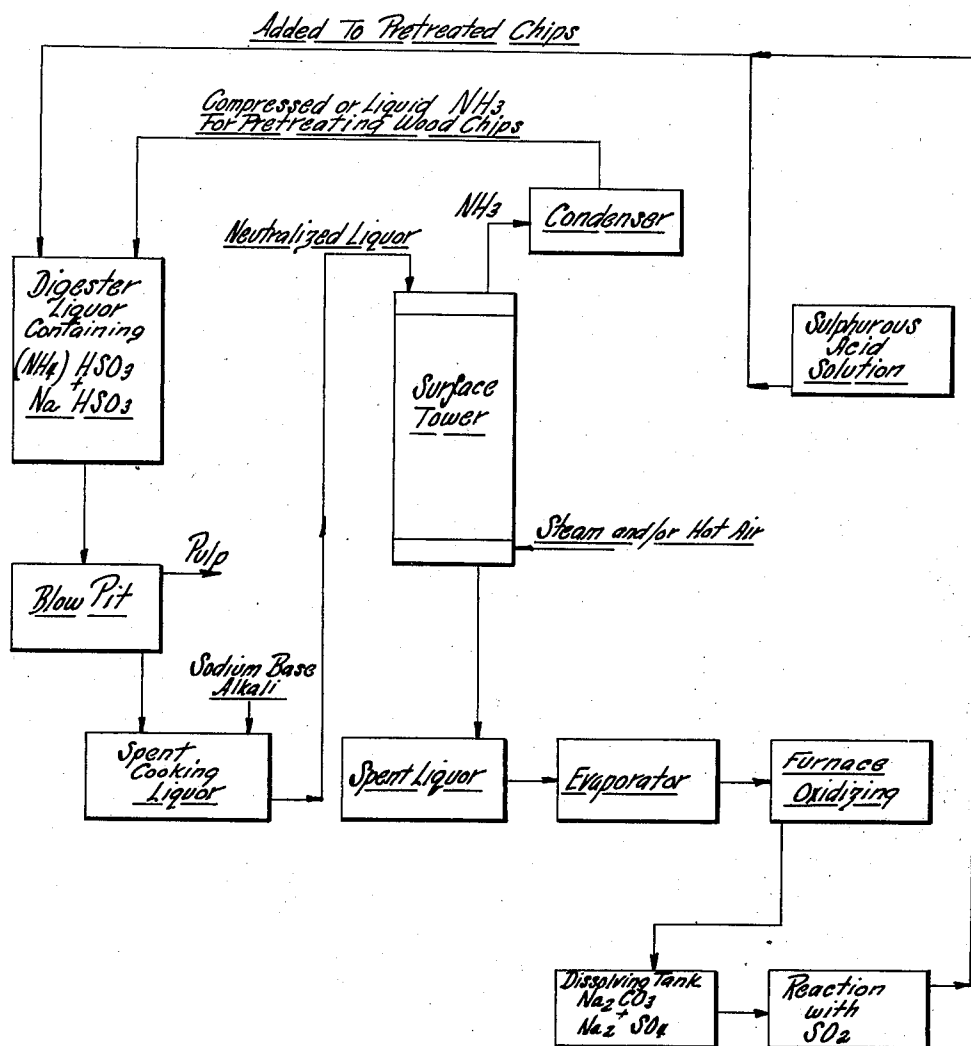
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FIBER LIBERATING PROCESS

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FIBER-LIBERATING PROCESS

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This invention relates to a fiber-liberating process, being more particularly concerned with the liberation of fiber from wood or other raw cellulosic material by the action of a sulphite or acid sulphite cooking liquor. While not limited there-
5 to, the process of the present invention will be described more specifically as applied to the pulping of wood.

It has been proposed to subject chipped wood to the fiber-liberating action of sulphite and/or acid sulphite cooking liquors, wherein ammonia in the form of the ammonium radical constitutes the basic element. Sulphite wood pulp produced by cooking under suitable conditions of temperature, pressure, time, and chemical concentration in such liquors are of a quality even excelling pulps prepared under comparable conditions in sulphite liquors containing calcium and/or sodium as the basic element. To be sure, ammonia is a more
10 expensive base than either calcium or sodium, but it is possible to operate commercially with an ammonia base sulphite liquor particularly when provision is made for recovering the ammonia constituent present in the spent ammonia base
15 sulphite liquors. For instance, the recovery of the ammonia constituent present in spent ammonia base sulphite cooking liquors may be correlated economically with the recovery of sodium constituent from spent sodium base alkaline
20 cooking liquors, such as so-called kraft and/or soda liquors, as disclosed in my application Serial No. 745,924, filed September 28, 1934.

The present invention devolves more particularly about the impregnation of the chipped wood
25 or other raw cellulosic material with fiber-liberating chemical in the form of ammonium sulphite and/or ammonium bisulphite preparatory to the cooking or fiber-liberating operation. The object of the present invention is to make possible the resolution of the chipped wood or other raw
30 cellulosic material into a high grade cellulose pulp in a minimum period of time and with a minimum usage of fiber-liberating chemical in the form of ammonium sulphite and/or ammonium bisulphite. Another objective is the use of a com-
35 posite base sulphite and/or bisulphite liquor comprising both ammonia and sodium as the basic elements and yielding spent cooking liquors from which the valuable ammonia and sodium con-
40 stituents may be easily recovered for reuse in the pulping of other raw cellulosic material.

In accordance with the present invention, the chipped wood or other raw cellulosic material to be resolved into cellulose pulp is impregnated
45 or permeated with ammonia fumes or vapors

while it is confined as a charge preferably in the very digester in which the pulping or cooking operation is to be performed. After the mass of raw cellulosic material has been substantially uniformly impregnated with gaseous ammonia in
5 sufficient amount, based on raw cellulosic material, to yield a cooking liquor of a combined SO_2 content capable of promoting the desired pulping or fiber-liberating action, a sulphurous acid solution is added to the confined ammoniated mass
10 to produce the ammonium sulphite and/or ammonium bisulphite cooking liquor of the appropriate combined SO_2 content in situ therein. Upon the addition of the sulphurous acid solution to the ammoniated mass, for instance, a charge
15 of wood chips confined in an ordinary sulphite digester, the sulphurous acid solution diffuses promptly into the pores and interstices of the wood wherein it immediately undergoes reaction
20 with the ammonia already present therein to form ammonium sulphite and/or bisulphite in situ therein. This means that fiber-liberating chemical has been introduced rapidly and uniformly
25 into and throughout the wood structure and, accordingly, that it is unnecessary to bring the charge slowly to fiber liberating or cooking temperatures for the purpose of distributing
30 fiber-liberating chemical substantially uniformly throughout the wood structure, as is customary practice. On the contrary, once the sulphurous acid solution has been added to the ammoniated charge, it is possible to heat
35 the charge rapidly to pulping or fiber-liberating temperatures while at the same time attaining substantially uniform pulping or fiber-liberating action throughout the chip structure
40 and producing substantially uniform pulp. By the practice of the present invention, it is hence possible to prepare a high grade sulphite pulp, such as is suitable for making papers and cellulose derivatives, in a period of time shorter than
45 that ordinarily required and/or with a liquor of a combined SO_2 content lower than that of the usual sulphite liquor. The expression "combined SO_2 content", as used herein means sulphur dioxide constituent existing in combination with the
50 base as the straight or neutral sulphite. In order words, the quoted expression is used herein in the sense customarily understood in the sulphite pulp-making industry, namely, as indicating sulphur dioxide constituent that is unavailable for neutralization with caustic soda or other alkali.

There are various ways in which the initial treatment of the woods chips with ammonia fumes may be performed accordant with my in-
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vention, the wood employed being of such varieties as spruce, birch, pine, fir, etc. Thus, gaseous ammonia under super-atmospheric pressure may be delivered from a suitable source of supply into
5 a closed sulphite digester charged with the wood chips, the amount of ammonia thus added being controlled so as to yield ultimately in the digester a cooking liquor of the appropriate composition. If desired, the air in the digester may be evacuated
10 before the introduction of the ammonia gas thereinto under atmospheric or super-atmospheric pressure, thereby avoiding dilution of the ammonia by air and also promoting a more rapid filling of the pores and interstices of the wood
15 chips with the ammonia gas. The wood chips may be in air-dry condition and thus contain, as ordinarily, about 30% of moisture, based on the bone-dry weight of the wood. The presence of moisture in the chips fosters a diffusion of
20 the ammonia fumes into, and an absorption of the ammonia by, the chips. If desired, the chips may be steamed or otherwise moistened prior to bringing the ammonia vapors into contact therewith, although, as already indicated, it is
25 possible to work with chips in air-dry or even drier condition. In some instances, the ammonia vapor and/or the chips to be treated therewith may be heated, as by the use of live steam, in which case, the steam may be introduced along
30 with the ammonia vapor and/or be applied directly to the chips.

An advantageous way of getting the ammonia gas into the pores and interstices of the chips is by injecting liquid ammonia into the closed
35 digester charged with the chips, the interior of the digester being under atmospheric or sub-atmospheric pressure. The liquid ammonia thus introduced into the closed digester immediately flashes into ammonia fumes which penetrate into
40 and throughout the mass of chips and chip body. The liquid ammonia may be introduced into the digester in amount and under temperature conditions to develop a pressure of, say, 20 to 100 pounds, in the digester. The liquid ammonia may
45 be added in amount greater than that necessary to yield a sulphite cooking liquor of the desired composition, whereupon, after the liquid ammonia has flashed into vapor, such excess ammonia as is present in the closed digester may
50 be released therefrom and recovered. Thus, the excess ammonia vapor may be permitted to escape from the digester into a suitable cooling and condensing system designed to re-liquefy the ammonia vapor for reuse.

55 Once the chips have been ammoniated to the desired degree, a sulphurous acid solution may be added to the closed digester containing the ammoniated chips. The amount of ammonia used in pretreating the chips and the amount of sulphurous acid solution added thereto may be
60 controlled to yield a cooking liquor containing in solution, say, about 0.5% to about 1.0% combined SO_2 and about 3% to 5% or more of free SO_2 . In this connection, it is to be observed that
65 the combined SO_2 values given for the cooking liquor are calculated ones that include combined SO_2 constituent that exists both in situ in the wood structure and in the free solution surrounding the chips. Indeed, if samples of the cooking
70 liquor were actually taken from the digester and tested for combined SO_2 content, the test would show a combined SO_2 content less than that given for the liquor. In other words, although the calculated combined SO_2 content existing in the
75 digester is given as ranging from, say, about 0.5%

to 1.0%, the combined SO_2 content existing inside the chips for a cooking liquor having a given calculated combined SO_2 content will be appreciably higher than such given calculated combined SO_2 content, particularly during the initial
5 stages of the cooking operation. Indeed, as already indicated, an important advantage of the practice of my invention resides in the maintenance of a comparatively high concentration of combined SO_2 within the wood structure
10 wherein it exercises the desired fiber-liberating action, so that only a comparatively small total combined SO_2 content, based on wood, may be relied upon to promote the desired pulping or fiber-liberating action. When combined SO_2 is
15 present in the liquor surrounding the chips to the same degree or concentration as exists in the chips, as in ordinary cooking practice, a much higher percentage of combined SO_2 , based on wood, must be present in the digester to produce
20 pulping or fiber-liberation by reason of the fact that the combined SO_2 in the liquor does not actually do any work of promoting pulping or fiber-liberation, simply serving as a reservoir for combined SO_2 from which the combined SO_2 necessary for pulping or fiber-liberating action diffuses
25 into and is absorbed by the chips. The digester contents may then be heated quickly to temperatures of about 240° to 300° F.; and cooking at such temperatures may be continued until complete fiber-liberation has been effected. Whereas
30 cooking by the usual sulphite process must be carried on for about ten hours to produce satisfactory pulp, it is necessary to cook wood chips in accordance with my invention for only about
35 six hours in producing highly satisfactory pulp. Thus, when cooking is performed at a temperature of about 275° F. or greater, the cooking period need be only about six hours. Of course, the cooking period may be longer when performed at lower temperatures, for instance, at
40 temperatures below about 245° F. In such latter instance, cooking may be continued at a temperature not exceeding 245° F. for a period of about 10 to 11 hours to produce pulp of unusually
45 good qualities and with greater yield of pulp than that ordinarily realized.

An important advantage attainable by the practice of the present invention is, as already indicated, the production of satisfactory pulp in a
50 sulphite cooking liquor containing less combined SO_2 than that present in the usual sulphite cooking liquor. Indeed, it is possible to effect satisfactory pulping of chipped wood in a liquor containing only about 2% to 4% combined SO_2 ,
55 based on the bone-dry weight of the wood, when the sulphur dioxide has been combined with the ammonia in situ in the chip body, as hereinbefore described, despite the fact that in usual sulphite cooking it is necessary to use a cooking liquor
60 containing as much as 8% or more combined SO_2 , based on the bone-dry weight of the wood. It is, of course, possible to practice my invention while employing liquors of a combined SO_2 content, based on wood, greater than that just cited. For
65 instance, it may be desirable to practice my invention in the production of a uniform but undercooked pulp of the variety that lends itself admirably to the manufacture of so-called glassine papers. In such latter instance, my invention
70 may be practiced while employing a liquor containing, say, 6% or more combined SO_2 , based on the bone-dry weight of wood, but less free SO_2 content than that present in the usual acid sulphite cooking liquors. Depending on such fac-
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tors as the concentration of the ammonia gas used in the pretreatment of the wood chips, the temperature and the pressure under which ammoniation is performed, the moisture content of the chips during ammoniation, the time of the pretreatment with the ammonia gas may vary from, say, ten minutes to four hours. Ordinarily, however, when liquid ammonia is introduced into the digester charged with the wood chips and caused to flash into ammonia vapor, as hereinbefore described, the period of ammoniation necessary to effect the desired impregnation of the chips is about 1 to 2 hours. To be sure, basic element in the form of ammonia is more expensive than basic element in the form of, say, sodium, but one molecular weight of sulphur dioxide, that is, 64 parts by weight of sulphur dioxide, requires for chemical combination therewith 106 parts by weight of sodium constituent in the form of soda ash but only 34 parts by weight of liquid ammonia. Inasmuch as it is possible, as already indicated, to pulp wood satisfactorily with much less ammonia base than with sodium base and inasmuch as a given combined SO₂ content in the cooking liquor is realized with much less weight of ammonia base than of sodium base, it is obvious that it may be economical to work with ammonia base even though such base is far more expensive than sodium base. For example, assuming that the ammonia base cooking liquor employed in accordance with my invention has a combined SO₂ content of 4%, whereas the ordinary sodium base cooking liquor has a combined SO₂ content of 8%, and assuming further that sodium constituent is available on the market in the form of soda ash at one cent per pound, calculation indicates the commercial feasibility of using liquid ammonia at five cents per pound. This calculation is made on the assumption that both the spent ammonia base and sodium base sulphite liquors are to be discarded or wasted. As already mentioned, however, it is possible to recover economically the ammonia constituent of spent ammonia base sulphite cooking liquor, particularly by a practice such as has been outlined in my aforementioned patent application.

In some instances, the cooking liquor employed according to the present invention may contain some sodium base as well as ammonia base. Thus, the sulphurous acid solution added to the ammoniated wood chips may contain dissolved therein sodium sulphite and/or sodium sulphate (salt cake) and/or sodium acid sulphate (niter cake); and, if desired, the sulphurous acid solution may contain some free sulphuric acid to form ammonium sulphate as well as ammonium sulphite in the cooking liquor. Rather than adding the sulphur dioxide to the ammoniated wood chips in the form of a sulphurous acid solution, it may be introduced into the closed digester charged with the ammoniated chips in the form of a gas or liquid in much the same manner as the ammonia is introduced. If desired, gaseous sulphur dioxide may be introduced into the digester in amount only sufficient to react with the ammonia existing largely inside the chips to form ammonium bisulphite in situ therein, whereupon such additional or free SO₂ as is desired in the cooking liquor during the cooking operation may be added to the digester in the form of a sulphurous acid solution which serves to cover partly or completely the chips during the cooking operation. It is thus seen that part of the sulphur dioxide may be added in gaseous form and part

as a sulphurous acid solution. After the ammonia and sulphur dioxide have reacted in the digester to form ammonium sulphite or while such reaction is taking place, water may be added to the digester in sufficient amount to cover partly or completely the chips and thus to permit their uniform cooking or pulping. The use of gaseous or liquid sulphur dioxide does away with the need for an absorption system such as is necessary for preparing a sulphurous acid solution and may, in some instances, be preferred practice.

In those instances when cooking is performed in a composite base sulphite liquor comprising sodium as well as ammonia base, the recovery of the valuable sodium and ammonium constituent from the spent sulphite cooking liquor may be effected to good advantage as illustrated by the flow-sheet on the accompanying drawing. As depicted in the flow-sheet, the chips may be pulped in a cooking liquor comprising a solution of ammonium acid sulphite and sodium acid sulphite and having the desired combined and free SO₂ contents. After cooking or pulping has been completed, the digester contents may, as ordinarily, be discharged or "blown" into a blow-pit wherein the spent cooking liquor may be separated, as by draining, from the pulp. The spent cooking liquor may then be treated with sufficient sodium base alkaline compound to be neutralized thereby. Neutralization of the liquor tends to liberate its ammonia content; and substantially all of the ammonia content of the neutralized liquor may be liberated and expelled therefrom by delivering the liquor downwardly through a tower into countercurrent contact with steam and/or hot air. The ammonia thus liberated may be recovered in compressed or liquid form and be employed in the pretreatment of the chips, as already described. The spent liquor delivered from the tower may be concentrated, as by multiple-effect evaporation, to a condition where its organic content may be readily burned and its inorganic content smelted. In such concentrated condition the liquor may be delivered into a furnace operated under oxidizing conditions wherein its organic content is consumed and its inorganic content smelted to produce a mixture of sodium carbonate and sodium sulphate. The mixed sodium carbonate and sodium sulphate smelt being substantially completely water-soluble may be dissolved in water to form a solution which may be caused to react with sulphur dioxide to produce a sodium base sulphite liquor. Such sodium base sulphite liquor may be commingled with the sulphurous acid solution that is added to the ammoniated wood chips in the digester. The ammonia liberated and recovered from the spent cooking liquor may, as previously stated, be used in the pretreatment of the wood chips. If desired, however, it may be caused to react with a sulphurous acid solution to form an ammonia base sulphite cooking liquor. The ammonia base sulphite cooking liquor may be commingled with the sodium base sulphite liquor to form the composite base cooking liquor delivered to the digester. If desired, both the recovered ammonia and the solution of smelted compounds may be caused to react simultaneously with sulphur dioxide to produce the composite base sulphite cooking liquor.

Inasmuch as there will be a tendency for the accretion of sodium constituent in the composite base sulphite cooking liquor on account of the use of sodium base alkaline compounds for the neutralization of the spent acid cooking liquor, pro-

vision may be made for the removal of sodium carbonate from the solution of the smelted compounds. Thus, sodium carbonate may be removed from such solution as by selective crystallization or by precipitating it with carbon dioxide as sodium bicarbonate, and the sodium carbonate or sodium bicarbonate thus removed used as the neutralizing agent for the spent composite base cooking liquor. However, it is preferable to causticize the sodium carbonate or sodium bicarbonate before neutralizing the spent composite base cooking liquor so as to avoid the dilution of the liberated ammonia gas with the simultaneously liberated carbon dioxide gas. The sodium sulphate and any residual sodium carbonate in the mother liquor may, if desired, be causticized preparatory to its reaction with sulphur dioxide. Causticization should be effected in those instances when it is preferable that the sodium base constituent be present in the cooking liquor in the form of sodium sulphite rather than sodium sulphate. Of course, only part of the sodium sulphate present in the mother liquor need be causticized, in which case the cooking liquor will contain ammonium sulphite and sodium constituent in the form of both sodium sulphite and sodium sulphate.

In order to ensure a substantially uniform distribution of the ammonia fumes as promptly as possible throughout a charge of wood chips in the digester, particularly a large-sized commercial unit, it may be desirable to introduce the ammonia fumes or the liquid ammonia into the digester at a number of properly spaced localities and/or to provide for positive circulation in the digester, as by a suction fan or pump that serves to withdraw gas from one end of the digester, i. e., the top or bottom, and discharge or inject it into the other end. When liquid ammonia is added to the digester, the heating of the digester contents, as by the introduction of live steam thereinto, may be desirable, as this promotes the vaporization of the ammonia and its diffusion throughout the charge of wood chips and the chip structure.

Inasmuch as acid sulphite liquors containing highly soluble sulphites, such as ammonium sulphite and sodium sulphite, are more severe in their chemical or erosive action on the brick linings of the usual commercial digesters than calcium base acid sulphite liquors, it may be desirable to add to the acid sulphite cooking liquors of the present invention containing the highly soluble ammonium sulphite such comparatively insoluble salts as calcium sulphate, barium sulphate, barium sulphite, or the like, in such amount that they occur in suspension in the cooking liquor surrounding the chips during the cooking operation. Such salts are usually objectionable in the cooking liquor during the cooking operation, as they tend to plug up the surface pores of the wood chips and thus to interfere with the desired penetration of combined SO_2 into the interior of the chips wherein combined SO_2 , that is, sulphite, is desired for the purpose of promoting fiber-liberation as quickly and uniformly as possible. In this connection, it might be observed that if wood chips were first soaked for a considerable period of time in an ordinary cooking liquor, such as a calcium bisulphite liquor, dissolved calcium bisulphite, i. e., combined SO_2 , would penetrate into the wood structure, but it is impossible to introduce into the wood structure by any commercially feasible practice of which I am aware substantially the entire quan-

tity of combined SO_2 that makes for substantially uniform and complete pulping or fiber-liberating action on the wood. Accordingly, in such latter instance, the suspension of insoluble salts, such as calcium sulphate, in the cooking liquor is attended by a retarded pulping or fiber-liberating action, as the insoluble salt in suspension interferes, as already indicated, with a diffusion into the chips of the combined SO_2 that is required for complete pulping or fiber-liberation from the cooking liquor serving as the reservoir for such combined SO_2 as is necessary for complete pulping or fiber-liberating action. In the practice of the present invention, on the other hand, substantially all of the combined SO_2 necessary for complete pulping or fiber-liberating action is introduced quickly and uniformly throughout the wood structure, as already stressed, wherefore, the concentration of combined SO_2 within the wood structure is appreciably higher, particularly during the initial stages of the cooking operation, than that of the cooking liquor surrounding the wood. When, however, combined SO_2 in the form of ammonium sulphite has been introduced in situ in and throughout the chip structure according to my invention, the presence of insoluble salt in suspension in the liquor surrounding the chips is not detrimental. The presence of insoluble alkaline earth metal salt, and more especially the sulphate, in suspension in the liquor surrounding the chips is of value in that such salt tends to deposit during the cooking operation as a scale or cake on the digester lining and thus to offset the chemical or erosive action that the acid sulphite liquor containing ammonium sulphite would otherwise have on the lining. In some instances, the cooking liquor of the present invention may be one containing besides ammonium bisulphite sufficient other bisulphite, such as calcium, and/or barium and/or strontium bisulphite, in solution therein, to precipitate the less soluble calcium sulphite and/or barium sulphite and/or strontium sulphite at the end of the cooking operation, that is, when free SO_2 is being released from the digester, as ordinarily, preparatory to the digester-blowing operation. In other words, the cooking liquor may be one containing little, if any, insoluble salt in suspension therein during most of the cooking operation but wherein insoluble salt is precipitated at the end stages of the cooking operation so as to deposit the desired protective layer of insoluble material on the digester lining.

For the sake of simplicity, I have described the cooking liquors of the present invention as having particular calculated combined SO_2 contents, despite the fact that most or practically all of the combined SO_2 , particularly during the initial stages of the cooking operation, may be present in the wood structure rather than in the liquor surrounding the wood chips. The appended claims have also been drafted in terms of such calculated combined SO_2 contents, that is, total combined SO_2 content present in the digester, irrespective of what fraction of the total combined SO_2 content exists in the wood structure and what fraction exists at any time in the cooking liquor surrounding the wood.

I claim:

1. A process of pulping raw cellulosic material which comprises impregnating a mass of such material while under confinement with ammonia fumes, adding sulphur dioxide and water to the ammoniated mass to form ammonium sulphite

pulping liquor in situ therein, and cooking the mass in the resulting liquor to form pulp.

2. A process of pulping raw cellulosic material which comprises premeating a mass of such material while under confinement with ammonia fumes, adding a sulphurous acid solution to the ammoniated sulphite pulp liquor in situ therein, and cooking the mass in the resulting liquor to form pulp.

3. A process of pulping raw cellulosic material which comprises ammoniating a mass of such material while under confinement with ammonia fumes at super-atmospheric pressure, adding a sulphurous acid solution to the ammoniated mass to form ammonium bisulphite pulping liquor in situ therein, and cooking the mass in the resulting liquor to form pulp.

4. A process of pulping raw cellulosic material which comprises adding liquid ammonia to a mass of such material while under confinement under conditions to cause the ammonia to flash into fumes and thereby to permeate such material, adding a sulphurous acid solution to the ammoniated mass to form ammonium sulphite cooking liquor in situ therein, and cooking the mass in the resulting liquor to form pulp.

5. A process of pulping chipped wood which comprises impregnating a mass of such wood while under confinement with ammonia fumes in such amount as to be capable of yielding a bisulphite cooking liquor of a combined SO_2 content not exceeding about 4%, based on the bone-dry weight of the wood, adding a sulphurous acid solution to the ammoniated wood to form ammonium bisulphite cooking liquor in situ therein, and cooking the wood in the resulting liquor to form pulp.

6. A process of pulping chipped wood which comprises impregnating a mass of such wood while under confinement with ammonia fumes in such amount as to be capable of yielding a bisulphite cooking liquor of a combined SO_2 content not exceeding about 4%, based on the bone-dry weight of the wood, adding a sulphurous acid solution to the ammoniated wood to form ammonium bisulphite cooking liquor of about 0.5% to 1.0% strength in situ therein, and cooking the wood in the resulting liquor to form pulp.

7. A process which comprises impregnating a mass of raw cellulosic material while under confinement with ammonia fumes, adding a sulphurous acid solution and sodium sulphite to the ammoniated mass to form a composite base sulphite pulping liquor containing ammonium sulphite and sodium sulphite as fiber-liberating chemicals, and cooking the mass in the resulting liquor to form pulp.

8. A process which comprises cooking raw cellulosic material in a chemical pulping liquor containing ammonium sulphite and sodium sulphite as fiber-liberating chemicals, separating the pulp from the resulting spent pulping liquor, adding sodium base alkaline compound to the spent pulping liquor under conditions to liberate its ammonia content, recovering the liberated ammonia, and recovering as a substantially completely water-soluble smelt the sodium constituent remaining in the spent pulping liquor.

9. A process which comprises impregnating a mass of raw cellulosic material while under confinement with ammonia fumes, adding a sulphurous acid solution and sodium sulphite to the ammoniated mass to form a composite base sulphite pulping liquor containing ammonium sulphite and sodium sulphite as fiber-liberating chemicals,

cooking the mass in the resulting liquor to form pulp, separating the pulp from the resulting spent pulping liquor, adding sodium base alkaline compound to the spent pulping liquor under conditions to liberate its ammonia content, and recovering the liberated ammonia for use in the impregnation of other raw cellulosic material.

10. A process which comprises impregnating a mass of raw cellulosic material while under confinement with ammonia fumes, adding a sulphurous acid solution and sodium sulphite to the ammoniated mass to form a composite base sulphite pulping liquor containing ammonium sulphite and sodium sulphite as fiber-liberating chemicals, cooking the mass in the resulting liquor to form pulp, separating the pulp from the resulting spent pulping liquor, adding sodium base alkaline compound to the spent pulping liquor under conditions to liberate its ammonia content, recovering the liberated ammonia for use in the impregnation of other raw cellulosic material, and recovering the sodium constituent remaining in the spent pulping liquor at least partly as a compound convertible by reaction with sulphurous acid into sodium sulphite, whereby sodium sulphite may be formed from said recovered sodium constituent for addition along with a sulphurous acid solution to other ammoniated raw cellulosic material to reproduce a fresh composite base sulphite pulping liquor.

11. A process which comprises impregnating a mass of raw cellulosic material while under confinement with ammonia fumes, adding a sulphurous acid solution and sodium sulphite to the ammoniated mass to form a composite base sulphite pulping liquor containing ammonium sulphite and sodium sulphite as fiber-liberating chemicals, cooking the mass in the resulting liquor to form pulp, separating the pulp from the resulting spent pulping liquor, adding sodium base alkaline compound to the spent pulping liquor under conditions to liberate its ammonia content, recovering the liberated ammonia for use in the impregnation of other raw cellulosic material, smelting the sodium constituent remaining in the spent pulping liquor under oxidizing conditions, and treating the smelted compounds with a sulphurous acid solution to produce a solution containing sodium sulphite for addition to other ammoniated raw cellulosic material and thereby to reproduce a fresh composite base sulphite pulping liquor.

12. A process which comprises cooking raw cellulosic material in a composite base sulphite pulping liquor containing ammonium sulphite and sodium sulphite as fiber-liberating chemicals, separating the pulp from the resulting spent pulping liquor, adding sodium base alkaline compound to the spent pulping liquor under conditions to liberate its ammonia content, recovering the liberated ammonia, recovering the sodium constituent remaining in the spent pulping liquor as a substantially completely water-soluble smelt and at least partly as a compound convertible by reaction with sulphurous acid into sodium sulphite, and causing said recovered ammonia and said recovered sodium constituent to react with a sulphurous acid solution to reproduce a fresh composite base sulphite pulping liquor.

13. A process which comprises cooking raw cellulosic material in a composite base sulphite pulping liquor containing ammonium sulphite and sodium sulphite as fiber-liberating chemicals, separating the pulp from the resulting spent pulping liquor, adding sodium base alkaline

compound to the spent pulping liquor, under conditions to liberate its ammonia content, recovering the liberated ammonia, recovering the sodium constituent remaining in the spent pulping liquor as a substantially completely water-soluble smelt and at least in part as sodium carbonate, and causing said recovered ammonia and said recovered sodium constituent to react with a sulphurous acid solution to reproduce a fresh composite base sulphite pulping liquor.

14. A process which comprises cooking raw cellulosic material in a composite base sulphite pulping liquor containing ammonium sulphite and sodium sulphite as fiber-liberating chemicals, separating the pulp from the resulting spent pulping liquor, adding sodium base alkaline compound to the spent pulping liquor under conditions to liberate its ammonia content, recovering the liberated ammonia, recovering the sodium constituent remaining in the spent pulping liquor as a substantially completely water-soluble smelt containing substantially only sodium base alkaline compound, using part of said recovered sodium base alkaline compound in treating spent pulping liquor to liberate its ammonia content, and causing the rest of said recovered sodium base alkaline compound and said recovered ammonia to react with a sulphurous acid solution to reproduce a fresh composite base sulphite pulping liquor.

15. A process which comprises pulping raw cellulosic material in an ammonium bisulphite cooking liquor containing in suspension therein alkaline earth metal salt of much lower solubility than calcium bisulphite.

16. A process which comprises impregnating wood chips with ammonium sulphite as a fiber-liberating chemical and then pulping such impregnated chips in a sulphurous acid solution containing alkaline earth metal salt in suspension therein.

17. A process which comprises ammoniating wood chips substantially uniformly throughout their structure, adding sulphur dioxide and water to the ammoniated wood chips to form ammoni-

um bisulphite in situ therein, and pulping the wood chips in the resulting solution in the presence of alkaline earth metal sulphate suspended in such solution.

18. A process of pulping chipped wood which comprises adding liquid ammonia to a mass of such wood while under confinement under conditions to cause the ammonia to flash into fumes and to develop a pressure of about 20 to 100 pounds, adding a sulphurous acid solution to the ammoniated mass to form in situ therein ammonium sulphite cooking liquor, and cooking the mass in the resulting liquor to form pulp.

19. A process of pulping chipped wood which comprises adding liquid ammonia to a mass of such wood while under confinement under conditions to cause the ammonia to flash into fumes and thereby to permeate the mass, adding a sulphurous acid solution to the ammoniated mass to form in situ therein a sulphite cooking liquor of about 0.5% to 1.0% combined SO₂ content, and cooking the mass in such liquor to form pulp.

20. A process of pulping chipped wood which comprises adding liquid ammonia to a mass of such wood while under confinement under conditions to cause the ammonia to flash into fumes and thereby to permeate the mass, adding a sulphurous acid solution to the ammoniated mass to form in situ therein a bisulphite cooking liquor of about 0.5% to 1.0% combined SO₂ content and of at least about 3% free SO₂ content, and cooking the mass in such liquor to form pulp.

21. A process of pulping chipped wood which comprises adding liquid ammonia to a mass of such wood while under confinement under conditions to cause the ammonia to flash into fumes and to develop a pressure of about 20 to 100 pounds, adding a sulphurous acid solution to the ammoniated mass to form in situ therein a bisulphite cooking liquor of about 0.5% to 1.0% combined SO₂ content and of at least about 3% free SO₂ content, and cooking the mass in such liquor to form pulp.

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