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TREATMENT OF SULPHITE-WOOD-PULP LIQUOR.

No Drawing.

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The process includes a number of steps, which are enumerated and explained below.

5 The first step consists of the collection of the sulphite waste liquors from the blow pits into which the sulphite pulp is discharged from the digesters. The liquor is drained from the pulp through a perforated bottom in the blow pits. If necessary or justified under the particular conditions most of the 10 liquor which may still cling to the fibrous pulp after drainage by virtue of capillarity may be displaced by the gradual addition of water, which is evenly distributed over the surface of the pulp mass.

15 In the second step these liquors while still hot are subjected to filtration through a filter capable of retaining any and all fibers and solids in suspension. These fibers are returned to the blow pit, and the clear liquor while still hot may or may not be sprayed 20 through a nozzle or nozzles into the atmosphere, according to the process which the liquors are subjected to for the recovery of organic constituents.

25 The third step in the process consists in the collection of these (sprayed or unsprayed) liquors, and subsequent treatment at a temperature of substantially not less than 80 to 85° centigrade, with the oxide or hydroxide 30 of an alkaline earth metal in a tank provided with an efficient agitator, until the loosely combined sulphur dioxide contained in the liquor is changed to the sulphite of the alkaline earth metal, and until the hydrogen ion 35 concentration of the liquor is substantially such as is designated by the symbol or expression $\text{pH}=9$. The first half or two-thirds (not more) of the required treatment may be done in some respects advantageously with 40 the equivalent amount of a carbonate of an alkaline earth metal, if this is desirable or cheaper, but the rate of reaction is affected unfavorably, the carbonate of an alkaline earth metal being considered an equivalent 45 and as such included in the claims. When using the oxide, it is always slaked, forming a hydroxide solution or suspension. The hydroxide is always furnished to the liquor in dissolved or suspended form.

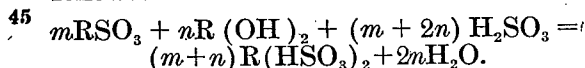
50 The selection of the alkaline earth metal oxide, hydroxide, or carbonate is governed by cost to a large extent, but disregarding this factor, or weighing it against the effectiveness of the result, the chemical considerations entering into the proposition are the 55 solubilities of the treating compounds, and

the solubilities of the products resulting therefrom. In this process it is most favorable chemically to use the compounds of those 60 alkaline earth metals which have the most soluble hydroxides, and which form the least soluble sulphites and sulphates. From these considerations it is apparent that in order of maximum to minimum desirability the alkaline earths should be arranged in the following 65 order, viz., barium, strontium, calcium, and magnesium. The comparatively low cost of lime, and the relative insolubility of its sulphate and sulphite make it quite satisfactory for the manufacture of a suitable 70 product at the present time. In step three one object is to accomplish principally three things, (1) the removal by conversion into insoluble form of some of the sulphur present, whether it be in the form of sulphites, 75 sulphates, sulphurous acid gas, or loosely combined and reversible sulphurous acid, (2) the change of the reaction of the liquor from acidic to basic, (3) the conversion into insoluble form of any such compounds which 80 would take place at much slower rate at lower temperature. It may be noted that the reagent used should contain only minimum amounts of iron.

The fourth step in the process consists in 85 filtering the insoluble matter produced in the third step from the resulting liquor. Complete separation is desirable, and the separated liquor should preferably be crystal clear. For this reason it is advisable to sub- 90 ject the liquor to sedimentation in any of the known forms of sedimentation or thickening apparatus, or simply in a tank, for a sufficient time to settle the major portion of the larger particles. The supernatant liquor is 95 drawn off and passed through a filter capable of holding the finest precipitates. While I do not limit this procedure to any particular form of filtration apparatus, it will be found preferable in most cases to use a high speed 100 centrifugal of the unperforated basket or bowl type, which discharges the clear liquid from the basket or bowl without passing it through the cake, which is precipitated in a compact mass on the side of the bowl or 105 basket, while the filtrate flows over the top of the basket or bowl, or out of the bottom. In step four some of the purposes are the minimizing of the decomposition of the liquor in its subsequent treatment for organic prod- 110 ucts recovery, the minimizing of corrosion of and deposition of scale on the surfaces of

any concentration apparatus in which the liquor is subsequently treated, and the production of a purer resulting concentrated product than if filtration were not resorted to, but one of the principal reasons for filtration is the recovery of these mineral solids, which it is the purpose of the invention to utilize in the preparation of the sulphite cooking liquor used in the beginning of the sulphite pulp manufacturing process, because of the alkaline earth metals and the sulphur these solids contain.

The fifth step covers the proper utilization of the above separated solids by adding them to sulphite cooking liquor in the course of its preparation. The chemical considerations involved are as follows: Regardless of the alkaline earth compound selected for the treatment in the third step, the residue, or at least the major portion of it, is soluble in sulphite liquor containing excess sulphurous acid, that is, in the cooking liquor or "acid" used in sulphite pulp manufacture. The sediment will contain more sulphite and less hydroxide if the alkaline earth metal compounds are chosen in the order named, i. e., progressing from barium to magnesium. Both the sulphite and the hydrate are valuable in the making of the cooking liquor, as by adding the sulphite to the liquor in the course of manufacture the soluble bisulphites are formed, and the equivalent amount of sulphur and alkaline earth metal base is saved over that used in the original preparation of the liquor. The hydroxide part of the sediment is valuable because these compounds unite with the sulphur dioxide gas used in the preparation of the cooking acid, forming the corresponding bisulphite compounds, effecting an equivalent saving in the alkaline earth base, usually limestone or lime, used in the cooking liquor preparation. These reactions may be expressed symbolically as follows:



In the above equation m and n are arbitrary numbers and R is the metal.

In practicing this step the sediment is conveyed by suspension in water, or any other method of conveyance to a tank, where it may be mixed with sulphite cooking liquor containing a considerable excess of free sulphurous acid, or may be treated along with the cooking liquor with the highly concentrated relief gas coming from the digesters. The tank may be so constructed and arranged that the whole mass is subjected to a mild stirring action. The tank may also be arranged that a mild pressure may be carried, to facilitate the reaction. The sulphurous acid present dissolves nearly all of the sediment, the insoluble matter remaining being of little or no value to the process.

The tank is also provided with a means of filtration or sedimentation, preferably the latter, so that these undesirable insoluble solids will not be carried along through the subsequent steps of the sulphite cooking liquor making process. The liquor, after sedimentation, is discharged from the tank ready for further use in the sulphite cooking process.

It is also to be noted that when barium or strontium is used, though only in amounts equivalent to a relatively small proportion of the total treating agent, an additional advantage is realized in that the sulphuric acid present in the cooking acid is precipitated as the very sparingly soluble sulphate, resulting in the removal of this acid from the sphere of action in the sulphite pulp cooking process. This sulphuric acid, while ordinarily conceived to be present in the combined form with lime (calcium sulphate) in the cooking liquors, acts as if in the free state, and in fact may partially exist in the free state, because of the effect of the far greater relative mass of free sulphurous acid present. In other words, in the cooking the sulphuric acid can at least in part come into play according to the following formula:



This sulphuric acid, at the high temperature at which it exists, exerts a hydrolytic action on the pulp in the sulphite digester, tending to weaken and soften it, and decrease the yield of the fiber. It has been the experience in the past that a better pulp was always obtained when sulphuric acid was present only in the smallest amounts possible.

The above procedure therefore clearly effects a considerable economy in the operation, and also offers some advantage in the improvement of the method of preparing the sulphite cooking liquors.

It is understood that the sulphite waste liquor which remained after the filtration in the fourth step, is to be further concentrated, or otherwise treated, and thereby converted into useful products, such as binders, adhesives, tanning extracts, etc., by any of the known processes, and it is furthermore understood that it is particularly adapted to the manufacture of a tanning extract by the process set forth in my patent application, Serial Number 539,284.

The present invention is not limited to the precise procedure herein set forth, because it will be obvious to those skilled in the art that modifications may be made in details, nor is the invention limited otherwise than as the prior art and the appended claims may require.

I claim:

1. In the treatment of wood pulp liquor the process which consists in recovering from the sulphite waste liquor solids useful in the

preparation of sulphite cooking liquor and containing principally sulphites insoluble in water by neutralizing the waste liquor with alkaline earth metal base sufficient to produce the degree of alkalinity expressed as pH=9 or greater alkalinity and sufficient to decompose the reversibly combined sulphurous acid present in combination with the substances dissolved from the wood to increase the recovery of the sulphur as monosulphite, and in the preparation of cooking liquor, treating the solids with cooking acid which contains free sulphurous acid for the conversion of the solids into soluble bisulphites.

2. In the treatment of wood pulp liquor the process which consists in recovering from the sulphite waste liquor solids containing principally sulphites insoluble in water by neutralizing the waste liquor with alkaline earth metal base sufficient to produce the degree of alkalinity expressed as pH=9 or greater alkalinity and sufficient to decompose the reversibly combined sulphurous acid present in combination with the substances dissolved from the wood to increase the recovery of the sulphur as monosulphite.

3. In the treatment of wood pulp liquor the process which consists in recovering from the sulphite waste liquor solids useful in the preparation of sulphite cooking liquor and including sulphites insoluble in water by neutralizing the waste liquor at substantially not less than 80 to 85° C. with alkaline earth metal base until the hydrogen ion concentration of the liquor is pH=9, or greater alkalinity and in the manufacture of cooking liquor treating the solids with sulphurous acid present in the cooking liquor for the conversion of the solids into soluble bisulphite.

4. In the treatment of wood pulp liquor the process which consists in recovering from the sulphite waste liquor solids including sulphites insoluble in water by neutralizing the waste liquor at substantially not less than 80 to 85° C. with alkaline earth metal base until the hydrogen ion concentration of the liquor is pH=9 or greater alkalinity.

5. In the treatment of wood pulp liquor

the process which consists in recovering from the sulphite waste liquor solids useful in the preparation of sulphite cooking liquor and including insoluble sulphites by neutralizing the waste liquor until the hydrogen ion concentration of the liquor is pH=9 or greater alkalinity and decomposing the reversible sulphurous acid present in combination with the substances dissolved from the wood to increase the recovery of the sulphur as monosulphite at substantially not less than 80 to 85° C. with alkaline earth metal compounds including some barium or strontium having basic deportment toward acid solutions and in the manufacture of the cooking liquor treating the solids with sulphurous acid present in the cooking liquor for the conversion of the solids into soluble bisulphites.

6. In the treatment of wood pulp liquor the process which consists in recovering from the sulphite waste liquor solids including insoluble sulphites by neutralizing the waste liquor until the hydrogen ion concentration of the liquor is pH=9 or greater alkalinity and decomposing the reversible sulphurous acid present in combination with the substances dissolved from the wood to increase the recovery of the sulphur as monosulphite at substantially not less than 80 to 85° C. with alkaline earth metal compounds having basic deportment toward acid solutions.

7. In the treatment of sulphite wood pulp liquor the process which consists in recovering from the waste liquor solids useful in the preparation of sulphite cooking liquor and in the elimination of the sulphuric acid ion from the sulphite cooking liquid by neutralizing the waste liquor with a base of alkaline earth metal of which the sulphite is insoluble in cooking liquor to at least the degree of alkalinity expressed as pH=9, and in the manufacture of the cooking liquor treating the solids with sulphurous acid present in the cooking liquor to convert them into soluble bisulphites which re-acting with the free sulphuric acid in the cooking liquor eliminate such acid therefrom.

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