

UNITED STATES PATENT OFFICE.

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RECOVERY OF VALUABLE PRODUCTS FROM SPENT SULPHITE LIQUORS.

No Drawing.

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This invention relates to the recovery of valuable products from spent digesting liquor, being more particularly related to the recovery of valuable products from spent liquors resulting from the digestion of cellulose-fiber-bearing material in sulphurous acid solutions of ammonium salts.

When cellulose-fiber-bearing material, such as wood, is digested in a sulphurous acid solution of a soluble sulphate and/or sulphite under prescribed conditions of time, temperature and chemical concentration, there is produced a sulphite pulp of low ash content, suitable for the manufacture of high grade papers and for the preparation of a high alpha-cellulose-containing fiber. When sodium sulphate and/or sodium sulphite are employed as the chemicals in the fiber-liberating sulphurous acid solution, the spent liquor resulting from digestion is separated from the pulp, neutralized preferably with basic sodium compounds, evaporated to the desired concentration, and then delivered to a combustion retort wherein its organic content is burned and its inorganic content smelted in a reducing or oxidizing atmosphere, depending on the chemicals which it is desired to recover. The smelted chemicals may be delivered from the retort into a body of water to produce a smelt solution which may then be subjected to further treatment for the preparation of an alkaline or acid digesting liquor, depending upon the conditions which were maintained in the retort. When, on the other hand, ammonium sulphate and/or ammonium sulphite are employed as the chemicals in the fiber-liberating sulphurous acid solution, the spent liquor resulting from digestion is separated from the pulp, but, in lieu of smelting the valuable combined nitrogen or ammonium compounds thereof as in the case of sodium compounds, is, in accordance with the process of the present invention, neutralized, preferably with basic calcium phosphate, and then evaporated to dryness but without smelting the ammonium compounds, for I have found that the residuum is admirably adapted for use as a fertilizer.

The spent liquor resulting from digestion in a sulphurous acid solution of ammonium salts contains fixed nitrogen in the form of the original salts, i. e., sulphate and sulphite, and also in the form of organic ammonium

compounds, as ammonium ligneous sulpho- nates. If digestion has been effected in a sulphurous acid solution of essentially only ammonium sulphate as described in my application, Serial No. 159,243, filed Jan. 5, 1927, because of the stability of the sulphate under digesting conditions, the resulting spent liquor contains substantially the fixed nitrogen content of the fresh digesting liquor. In addition, the liquor also contains the nitrogen and potassium removed from the wood during digestion. After the separation of the pulp from the spent liquor, such liquor is neutralized, preferably with basic calcium phosphate, so as to increase the fertilizing value of the product as well as to produce a neutral liquor which will not corrode apparatus in which it is subsequently processed. The neutral liquor is then evaporated to the desired concentration and finally dried to form a flaky or pulverulent residuum. Such a flaky or pulverulent residuum is suitable for sale as a fertilizer, not only because of its finely divided physical condition, but also because the fertilizing elements therein exist in a form readily available for plant nutrition.

A specific example of procedure which may be followed in producing the product of the present invention may be substantially as follows. After completing digestion in a sulphurous acid solution of an ammonium salt, i. e., ammonium sulphate and/or ammonium sulphite, the digester contents are blown in a blowpit. Chemicals such as SO_2 , which are emitted from the blow, may be recovered, if desired, by any approved method. The pulp is separated from the spent liquor and may then be subjected to such further processing as may be desired.

The separated acid spent liquor is then neutralized prior to the evaporation of a portion of its aqueous content, such neutralization preferably being effected with basic calcium phosphate rock. Such rock is readily obtainable on the market and not only serves as a relatively inexpensive neutralizing agent, but also as an excellent and inexpensive fertilizer-phosphorus-supplying material, for the sulphurous acid reacts with such basic phosphate to produce phosphates which are good plant nutritives. Preferably such phosphate is ground to a more or less pulverulent condition to promote

a rapid neutralizing action with the acid content of the spent liquor.

In certain instances where it is desirable to increase the potassium content of the product available as fertilizer, a potassium compound which reacts to form a plant nutritive, or which in itself without reaction serves as a plant nutritive, is added to the spent liquor. Preferably, a basic potassium compound, such as potassium carbonate, which acts as a neutralizing agent and forms a plant-nutritive salt, is employed as the potassium-supplying compound. The addition of such potassium compound to the acid spent liquor may be effected together with the addition of the basic phosphate.

The neutral spent liquor is evaporated to, say, about a 50% concentration, as by means of multiple-effect evaporators, whereupon the concentrate is delivered to a drum dryer, a hot air spray dryer, or other suitable form of drying apparatus, which removes the water content of the concentrate and produces a flaky or pulverulent residuum. Such a residuum is in suitable form for sale as a fertilizer, the fertilizing elements, viz, fixed nitrogen, phosphorus and potassium, existing therein in a form available as plant nutrients. It also contains the organic encrusting matter removed from the wood chips, such organic material enhancing its fertilizing value by decomposition in the soil into humus, carbon dioxide, and other products which stimulate plant growth and maintain the soil in a loose, porous condition.

In lieu of adding potassium-bearing material to the spent liquor, if desired, such material, e. g., potassium carbonate or potassium sulphate, may be employed together with the ammonium salts in the fresh sulphurous acid digesting solution. Also, a certain amount of phosphorus-bearing material, e. g., basic calcium phosphate, may be added, together with such potassium-bearing material. Potassium carbonate reacts with the free sulphurous acid to form potassium bisulphite, which functions as an excellent fiber-liberating agent, being equivalent in this respect to sodium bisulphite. Potassium sulphate remains essentially as such in the digesting liquor, only a small proportion thereof initially being converted to potassium bisulphite by metathetical reaction with the sulphurous acid, but as the potassium bisulphite is progressively consumed or spent by reaction, more potassium sulphate is progressively converted into potassium bisulphite. Basic calcium phosphate reacts with the sulphurous acid solution to form superphosphates and calcium bisulphite. The superphosphate is probably an inactive constituent of the cooking liquor, but the phosphorous constituent therein is in a form available for plant nutrition and ap-

pears in such form in the spent cooking liquor. The calcium bisulphite is, of course, an active fiber-liberating agent. The spent liquor resulting from digestion is neutralized, concentrated, and then dried to form a flaky or pulverulent product, as hereinbefore outlined.

A process such as herein described permits digestion of cellulose-fiber-containing material to be carried out on a practical commercial scale in sulphurous acid solutions of ammonium salts, since the valuable fixed nitrogen content of the fresh digesting liquor may be economically recovered from the spent digesting liquor and in addition economically fortified by other fertilizer elements, such as phosphorus and potassium. When digestion takes place in a sulphurous acid solution of essentially only ammonium sulphate, the spent liquor contains substantially the equivalent of the fixed nitrogen content of the fresh cooking liquor, as ammonium sulphate is substantially stable at digesting temperatures. Such nitrogen content of the spent liquor is augmented by the potassium and nitrogen content removed from the cellulose-fiber-bearing material. The process of the present invention eliminates the necessity of smelting and associated recovery apparatus necessary when digestion is effected in sodium salts, and also makes possible the production of sulphite pulp without necessitating the pollution of streams or rivers, such as takes place when digestion is carried out in calcium bisulphite liquors, the spent liquors from such latter process of digestion being largely wasted by discharge into flowing water and injuring piscatorial life and constituting a general nuisance.

I do not herein claim the process of digesting cellulose-fiber-containing material in sulphurous acid solutions of ammonium sulphate, as this is disclosed and claimed in my application for patent hereinbefore referred to.

What I claim is:

1. A fertilizer comprising the residuum of spent liquor resulting from the digestion of cellulosic material in a sulphurous acid solution of ammonium salts, said residuum including substantially all the organic matter removed from such cellulosic material.

2. A fertilizer comprising the residuum of spent liquor resulting from digestion of raw cellulosic material in a sulphurous acid solution of ammonium sulphate, said residuum including substantially all the organic matter removed from such cellulosic material.

3. A fertilizer comprising the residuum of spent liquor resulting from digestion of raw cellulosic material in a sulphurous acid solution of ammonium sulphate and ammonium sulphite, said residuum including

substantially all the organic matter removed from such cellulosic material.

4. A fertilizer comprising the residuum of spent liquor resulting from digestion of raw cellulosic material in a sulphurous acid solution of ammonium salts and containing potassium-containing material, said residuum including substantially all the organic matter removed from such cellulosic material.

5. A fertilizer comprising the residuum of spent liquor resulting from digestion of raw cellulosic material in a sulphurous acid solution of ammonium salts and containing phosphorous-containing material, said residuum including substantially all the organic matter removed from such cellulosic material.

6. A fertilizer comprising the residuum of spent liquor resulting from digestion of cellulosic material in a sulphurous acid solution of ammonium salts and containing potassium-containing material and phosphorus-containing material, said residuum including substantially all the organic matter removed from such cellulosic material.

7. A fertilizer comprising the residuum of spent liquor resulting from digestion of cellulosic material in a sulphurous acid solution of ammonium salts and neutralized with basic calcium phosphate.

8. A fertilizer comprising the residuum of spent liquor resulting from digestion of cellulosic material in a sulphurous acid solution of ammonium salts and neutralized with basic calcium phosphate and treated with potassium-containing material.

9. A fertilizer comprising the residuum of spent liquor resulting from digestion of cellulosic material in a sulphurous acid solution of ammonium salts and neutralized

with basic calcium phosphate and basic potassium-containing material.

10. A process which comprises neutralizing the spent liquor resulting from digestion of cellulosic material in a sulphurous acid solution of ammonium salts with basic calcium phosphate, evaporating and drying the neutralized liquor, and recovering the residuum.

11. A process which comprises neutralizing spent liquor resulting from digestion of raw cellulosic material in a sulphurous acid solution of ammonium salts, treating the spent acid liquor with basic calcium phosphate and potassium-containing material, evaporating and drying the neutralized liquor, and recovering the residuum.

12. A process which comprises neutralizing spent liquor resulting from digestion of raw cellulosic material in a sulphurous acid solution of ammonium salts with basic calcium phosphate and basic potassium compounds, evaporating and drying the neutral liquor, and recovering the residuum.

13. A process which comprises neutralizing spent liquor resulting from digestion of cellulosic material in a sulphurous acid solution of ammonium salts with basic calcium phosphate, evaporating and drying the neutralized liquor to produce a pulverulent or flaky residuum, and recovering the residuum.

14. A process which comprises neutralizing with basic calcium phosphate spent liquor resulting from digestion of cellulosic material in an acid solution of ammonium salts, and recovering the solids content of the neutralized liquor.

In testimony whereof I have affixed my signature.

GEORGE A. RICHTER.