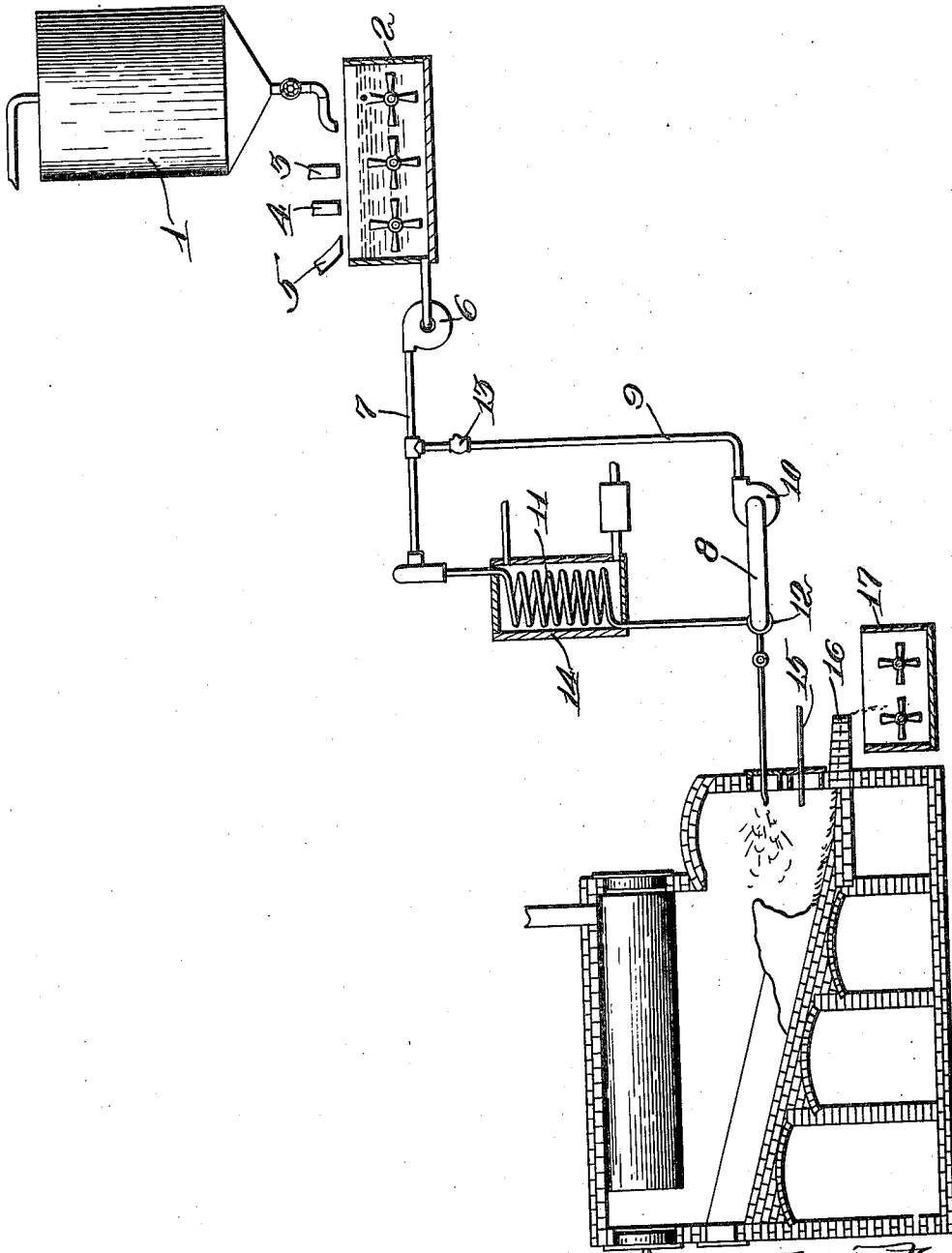


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PROCESS OF TREATING BLACK LIQUOR PRODUCED IN THE MANUFACTURE
OF SULPHATE PULP
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UNITED STATES PATENT OFFICE.

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PROCESS OF TREATING BLACK LIQUOR PRODUCED IN THE MANUFACTURE OF SULPHATE PULP.

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To all whom it may concern:

Be it known that we, GEORGE A. RICHTER and DOUGLAS H. McMURTRIE, citizens of the United States, residing at Berlin, in the
5 county of Coos and State of New Hampshire, have invented new and useful Improvements in Processes of Treating Black Liquor Produced in the Manufacture of Sulphate Pulp, of which the following is a specification.

10 The present invention relates generally to the manufacture of chemical wood pulp by the sulphate process, and more especially to the preparation of the cooking liquor employed for digesting the wood.

15 The name "sulphate" pulp or "sulphate" process ascribed thereto arises from the fact that heretofore it has been the practice to employ sodium sulphate for the purpose of producing sodium sulphide, by reduction, in
20 the smelting operation which forms a part of the process followed in the preparation of the cooking liquor.

In the ordinary method of preparing the cooking liquor, which includes the recovery
25 of the soda content of the black liquor, resulting from a previous digestion or cooking operation after it has been separated from the pulp, it has been customary by evaporation to concentrate the black liquor to a more or
30 less viscous condition, and then to add thereto, either while the liquor is in a liquid form or after it has been more or less charred, a certain proportion of sodium sulphate, and smelt the mixture in a smelting furnace. By
35 this smelting of the mixture of the sodium carbonate, sodium sulphate, the organic matter contained in the black liquor, and the remaining soda content of such liquor, the sodium sulphate is reduced to sodium sulphide in a reducing atmosphere, and the
40 "melt" or molten material, flowing from the furnace, consists principally of sodium sulphide and sodium carbonate, with more or less sodium hydroxide and unreduced sodium sulphate. This melt is received in a bath
45 of water, preferably more or less alkaline, and forms a solution. Subsequently lime is added thereto in the causticizing tanks to convert the sodium carbonate to sodium hydroxide, and the precipitated calcium carbonate is removed by filtration or otherwise.
50 The filtrate or remaining solution, which forms the liquor for digesting the wood in

a subsequent cooking operation, contains, essentially, sodium hydroxide and sodium sulphide, together with some unconverted sodium carbonate, sodium sulphate, and adventitious or foreign matter.

The especial object of the present invention is to produce a cooking liquor having a high predetermined sodium sulphide content. We have discovered that, by the addition of free sulphur to the black liquor to be consumed for the recovery of the soda content (either in a viscous or charred state), we are
65 able to fix the same as sodium sulphide, and thus to increase to a predetermined extent the proportion of sodium sulphide in the effluent from the smelting furnace.

For satisfactory results, the cooking liquor should comprise both caustic soda and sodium sulphide, in about the proportions of 7 to 3 based in terms of total alkali. Hence it is customary, in the usual recovery processes, to make up losses in total amount of
75 alkali by the addition of sodium sulphate, which is converted to sodium sulphide and sodium carbonate in the smelting operation. Depending upon the reduction, in the furnace, variable results are secured, and the effluent varies in the ratio of sodium carbonate to sodium sulphide.

By our process, which is hereinafter described, we secure a direct control, by introducing sulphur separately and not fixed
85 solely as sodium sulphate. In addition, we may also introduce sodium carbonate into the mixture to be smelted, or during the causticizing operation of the recovered "melt", thereby securing independent control
90 of each constituent.

These two materials Na_2CO_3 and S, may be used together with, or as a substitute for, the usual salt cake, Na_2SO_4 . In other words, we may eliminate the addition of sodium sulphate, in the recovery process, or may employ therewith free sulphur, and, if necessary, sodium carbonate. Thus the free sulphur may be substituted directly for the combined sulphur contained in the salt cake, or may be
100 added to increase the proportion of total sulphur to total sodium content, thereby increasing the proportion of sodium sulphide to sodium carbonate in the melt leaving the smelting furnace.

For example, with concentrated spent
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black liquor of about 32° Baumé, we mix the requisite amount of sulphur in a finely comminuted form, to produce a suitable quantity of sodium sulphide in the cooking liquor. In ordinary practice, the addition of sulphur in the proportion of 1% to 3% by weight of concentrated black liquor produces satisfactory results. The mixture may be exploded in a combined boiler and smelting furnace, by the process and apparatus set forth in U. S. Letters Patent No. 1,326,414, granted December 30, 1919, to Hugh K. Moore and John T. Quinn. If desired, however, the sulphur in solid or molten form may be introduced into the black ash resulting from the disk-evaporation and the charring in a rotary kiln or drum of the spent black liquor, or it may be introduced into the smelting furnace for admixture therein with the inorganic content of the black liquor.

The fixation of the sulphur as sodium sulphide, by the alkaline content of the black liquor, may result in a deficiency in sodium carbonate in the melt, and this deficiency may be made up by adding a suitable amount of sodium carbonate to the liquor before the causticizing operation. For example, we add an amount of sodium carbonate as determined by proportion from the chemically equivalent weights of sodium carbonate and sulphur,—namely 106 to 32. The sodium carbonate, however, may be mixed with the concentrated black liquor or introduced directly into the smelting furnace.

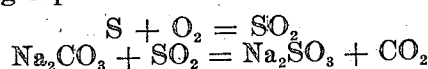
Again, free sulphur may be introduced into the black liquor together with a suitable quantity of sodium sulphate. For example, we have secured excellent results, by the addition of from 20 to 30 pounds of comminuted sulphur per ton of produced pulp, in which about 400 pounds of sodium sulphate per ton of pulp were used. In this case there was maintained in the cooking liquor a desirable high sulphidity.

The effluent from the smelting furnace is received as ordinarily in water or an alkaline bath, and the solution, after being causticized, and decanted or filtered, is employed for the digestion of wood in the manufacture of sulphate pulp. The spent black liquor, resulting from the digestion, is then evaporated to concentrated form, and the herein described cycle of operations is repeated.

On the accompanying drawing we have shown more or less conventionally and diagrammatically, a soda recovery system substantially as illustrated in the Letters Patent hereinbefore referred to by which we have carried out our process. In this particular system which has been selected only for purposes of illustrating one form which may be used, but to which we are not

limited, the concentrated black liquor is delivered from a storage tank 1 into a mixing vat 2 into which powdered free sulphur is delivered as desired from a spout 3. Sodium sulphate and sodium carbonate may be delivered as required into the mixing vat from spouts 4 and 5 respectively. The mixture is pumped by a pump 6 under high pressure through a circulating system comprising the conduits 7, 8, 9, the pump 10, coil 11, manifold 12, and check valve 13. The coil 11 is within a heater 14 by which the mixture is heated to a high temperature so as to generate an explosive force therein, the pressure on such mixture being greater than the vapor pressure. From the manifold 12, nozzles lead into the front of the furnace, so as to discharge the mixture into the upper portion of the combustion chamber. For supporting the combustion and producing an oxidizing atmosphere in the upper part of the chamber, air pipes 15 or tuyères extend into the furnace for delivering air thereto, under pressure if desired. A reducing atmosphere of carbon monoxide is created in the lower portion of the combustion chamber near the sloping floor wherein the molten soda flows forwardly and is delivered through one or more spouts 16 into a mixing vat or tank 17.

While we do not desire to be committed to any theory of operation or reaction, we have reason to believe that the first reaction, involving the sulphur sprayed with the black liquor into the furnace, is the oxidation of the sulphur to SO₂ and that thereupon the sulphur dioxide reacts with the sodium carbonate recovered with the black liquor (or added thereto if desired), such reactions being represented as follows:—



Inasmuch as there is an oxidizing atmosphere in the upper part of the furnace where the mixture is delivered and exploded, it may, perhaps, be fairly assumed that part of the SO₂ is converted to sodium sulphate (Na₂SO₄), due to the further oxidation of sodium sulphite (Na₂SO₃). The sodium sulphite and sodium sulphate reaching the floor of the furnace, are reduced to sodium sulphide.

It is also possible, and indeed probable, that since the concentrated black liquor contains caustic soda, part of the sulphur may react directly therewith, forming sodium sulphide and sulph-hydrate, but if so, doubtless this side reaction involves only a small part of the sulphur. If portions of the sulphur are not burned in the upper part of the combustion chamber and reach the floor of the furnace as free sulphur they, no doubt, react with such sodium carbonate or sodium hydroxide as may be pres-

ent to form sodium sulphide. We regard it as highly desirable in the use of a furnace as herein described that the sulphur should enter an oxidizing atmosphere first, and that there should also be a reducing zone in the furnace, in order that any sodium sulphite or sodium sulphate formed should be reduced to the sulphide.

What we claim is:—

- 10 1. A process comprising burning and smelting spent black liquor resulting from the digestion of wood in the manufacture of sulphate pulp, in the presence of free sulphur, and recovering the molten effluent.
- 15 2. A process comprising concentrating the black liquor resulting from the digestion of wood in the manufacture of sulphate pulp, adding free sulphur thereto, smelting the mixture, and recovering the molten effluent.
- 20 3. A process comprising concentrating the black liquor resulting from the digestion of wood in the manufacture of sulphate pulp and containing residual sodium carbonate, adding sulphur thereto, smelting the mixture, recovering the molten effluent containing sodium sulphide resulting from the reaction of sulphur with such sodium carbonate, and adding sodium carbonate in sufficient

quantities to compensate for the loss thereof by the chemical reaction of sulphur with sodium carbonate initially in the spent liquor.

4. The herein described process which comprises concentrating black liquor containing residual sodium carbonate, mixing free sulphur and sodium sulphate therewith, smelting the mixture, and recovering the molten effluent with a predetermined percentage of sodium sulphide.

5. The herein described process which comprises concentrating black liquor containing residual sodium carbonate, mixing free sulphur and sodium carbonate therewith, smelting the mixture, and recovering the molten effluent.

6. The herein described process which comprises concentrating black liquor containing residual sodium carbonate, mixing free sulphur, sodium carbonate and sodium sulphate therewith, smelting the mixture, and recovering the molten effluent.

In testimony whereof we have affixed our signatures.

GEORGE A. RICHTER.
DOUGLAS H. McMURTRIE.