

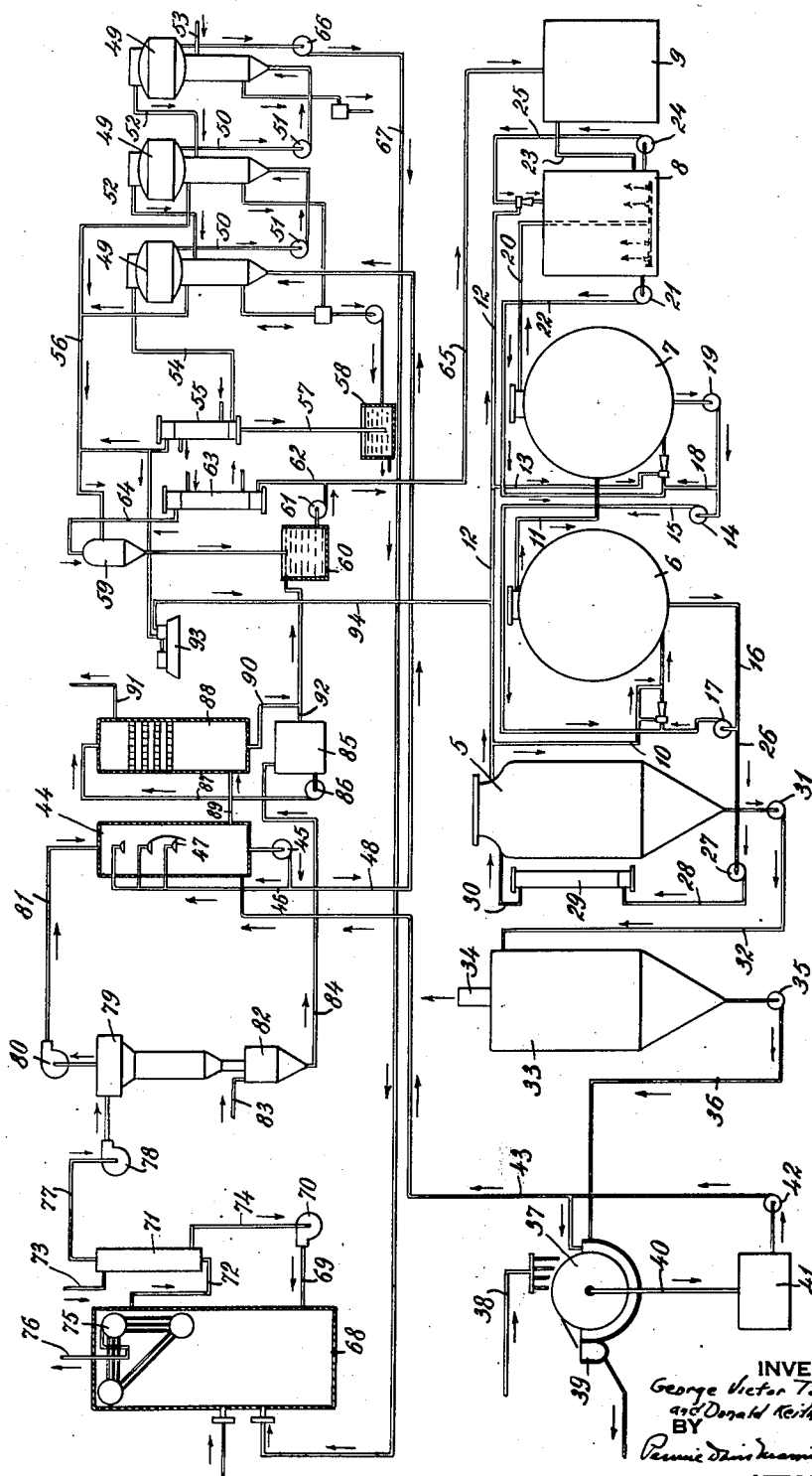
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SULPHITE PROCESS

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SULPHITE PROCESS

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This invention relates to the acid sulphite pulping process and particularly to improvements relating to the economy of such operations and the recovery of material from the waste liquor which may be reutilized in the process.

In a co-pending application Serial No. 326,843, filed March 30, 1940, it is shown that the Norwegian Patent No. 40,517 issued December 8, 1924, fails to disclose a practical and commercial operation. This patent suggests the use of magnesium sulphite as a cooking liquor in the sulphite process to produce a waste sulphite liquor which may be evaporated to dryness and burned. The resulting magnesium oxide may then be combined with sulphur dioxide from the combustion gases to produce magnesium sulphite liquor. The disclosure is defective in that it fails to take account of the necessity for providing a large proportion of free sulphur dioxide in the liquor used as a cooking medium, and no provision is made for the introduction of free sulphur dioxide to the magnesium sulphite liquor. The process as described in the Norwegian patent has never been practised commercially, and so far as is known the problems which arise in attempting to apply the procedure have not been considered or solved in a practicable manner.

The application aforesaid emphasizes the necessity for providing free sulphur dioxide in the cooking liquor. While the free sulphur dioxide does not enter directly into the reaction, it nevertheless exerts a driving force which speeds up the hydrolysis and sulphonation of the lignin and accomplishes the liberation of the cellulose much more rapidly and at lower temperatures than is otherwise possible. That application also indicates that the necessary free sulphur dioxide can be supplied to the cooking liquor by absorbing the sulphur dioxide relieved from the digester during and after the cooking operation, and that losses incident to the operation may be made up by the introduction of sulphur dioxide supplied by a sulphur burner, the gases from which normally carry approximately 14–18% of sulphur dioxide.

It is the object of the present invention to afford further improvements in the sulphite process based upon the theory of the Norwegian patent and adapted to permit the commercial practice of the procedure and the attainment of advantages resulting from its practical application.

Another object of the invention is the provision of a sulphite process in which waste products are consumed to permit regeneration of the cook-

ing liquor, including the provision of a liquor of the necessary strength in respect to combined and free sulphur dioxide, and permitting the recovery of sulphur dioxide which otherwise would be lost in the evaporation of the waste liquor prior to burning thereof.

Other objects and advantages of the invention will be apparent as it is better understood by reference to the following specification and the accompanying drawing, which illustrates diagrammatically apparatus suitable for the application of the process in commercial operations. Details of the structure are eliminated for the purpose of clarity.

When ligno-cellulose material is heated with an acid sulphite liquor, the reaction is one of hydrolysis, in which the bond between the lignin and the hemi-celluloses or cellulose is broken. This reaction is followed almost immediately by sulphonation of the lignin to form ligno-sulphonic acid which, if allowed to exist in the free state, results in the hydrolysis of the ligno-cellulose compounds too rapidly, with the result that the lignin polymerizes and is no longer capable of forming soluble sulphonic acid. In the presence of a base such as calcium, magnesium or sodium, present as a bisulphite compound, the metal ion combines with the ligno-sulphonic acid as fast as it is formed to produce a metal salt of the sulphonic acid. The reaction involving hydrolysis and sulphonation will then proceed smoothly, and a cellulose relatively free from polymerized lignin will be produced.

Experience has shown that in relation to the charge of wood on a bone dry basis, a definite minimum ratio of sulphur dioxide combined with the metal ion must exist in order to secure satisfactory pulping. This ratio for coniferous woods has been found to lie between .04 and .055 pounds of sulphur dioxide combined with the metal per pound of wood on the bone dry basis. While it is possible to cook wood and to liberate the cellulose therefrom with a metal bisulphite of such concentration that the sulphur dioxide is combined with the metal in the ratio mentioned, the cooking operation is relatively slow, and high temperatures are necessary. Both of the latter conditions are undesirable in a commercial operation, because of the cost and for other reasons.

To permit rapid cooking at lower temperatures, it is necessary, as already indicated, to provide free or uncombined sulphur dioxide in the cooking liquor. All of this free sulphur dioxide which is essential to the practical commercial operation of the sulphite process, is eventually relieved from

the digester, either during the cooking operation or at the termination thereof. It is necessary to provide, therefore, for the constant circulation of a large quantity of free sulphur dioxide between the digester and the fresh cooking liquor which is introduced thereto. Waste of sulphur dioxide must be avoided, so far as is practicable.

There is inevitably some loss of free sulphur dioxide in operations conducted under the best possible conditions. We have discovered that a particular source of such losses in the process contemplated results from the partial decomposition of organic sulphur compounds when the acid waste liquor is evaporated. This waste liquor, at the conclusion of the cooking operation, contains substantially no free sulphur dioxide if the digester pressure has been reduced to normal atmospheric pressure before the liquor and pulp are removed from the digester. However, when the waste liquor is subjected to vacuum evaporation in order to produce a concentrated waste liquor which may be burned to recover sulphur dioxide, the base and heat, there results in the evaporator a partial decomposition of the organic sulphur compounds, and we have found that the amount of sulphur dioxide relieved in the course of such evaporation amounts to 0.3 to 0.4 pounds of sulphur dioxide per hundred pounds of water evaporated. This represents a considerable proportion, from 10 to 20%, of the total sulphur recoverable from the waste liquor.

The sulphur dioxide which is freed from the organic compounds during evaporation may be recovered readily by condensing the vapors from the evaporating system. A suitable heat exchanger, through which the vapors may be conducted, cools them sufficiently to condense and remove the bulk of the water therein, leaving sulphur dioxide which may be utilized advantageously to fortify the sulphite liquor, affording a part of the free sulphur dioxide which must be necessarily provided therein before the liquor is utilized for cooking in the digester. This sulphur dioxide recovered from evaporation of the waste liquor, together with the sulphur dioxide relieved from the digester during and after the cooking operation, is sufficient usually to maintain the cooking liquor at the required strength. It is possible to make suitable additions, both of sulphur dioxide and of the base employed, to meet any losses which may occur in the system. This is best accomplished by introducing magnesium salts and sulphur in the required proportions into the combustion chamber when the evaporated liquor is burned.

The procedure as described solves practicably and in the manner to afford a commercially economical operation, the problems incident to a sulphite process in which magnesia is used as a base, so that the waste liquor can be burned and the magnesium oxide ash can be recombined with sulphur dioxide recovered in the system to afford a satisfactory cooking liquor. The resulting process is adapted to effect very substantial savings in the operation of the sulphite process, and particularly to avoid the discharge of undesirable waste products to the atmosphere and to streams which have been polluted heretofore by the discharge of waste products from sulphite plants.

Referring to the drawing, 5 indicates a digester of the usual type. The details of such a structure are well known and require no description. The digester is adapted to be supplied at intervals with ligno-cellulose material and with a cooking liquor consisting of magne-

slum bisulphite containing the desired ratio of combined sulphur dioxide and sufficient free sulphur dioxide absorbed therein to permit the rapid completion of the cook and the satisfactory recovery of cellulose.

To afford this cooking liquor, we provide storage vessels 6, 7, 8 and 9, the first two being pressure vessels. During the cooking operation which is conducted at pressures usually between 70 and 90 pounds per square inch, a certain amount of free sulphur dioxide is relieved from the digester 5 and is conducted by a pipe 10 into the vessel 6 where it is absorbed in the strong cooking liquor. Any surplus of sulphur dioxide not absorbed in the first vessel is conducted by a pipe 11 to the second vessel 7 which likewise receives sulphur dioxide relieved from the digester after the conclusion of the cook at pressures from 50 pounds down to 15 pounds per square inch through pipes 12 and 13. The vessel 7 contains the weaker liquor which is eventually delivered to the vessel 6 through a pump 14 and pipe 15. Circulation of the liquor in the vessels 6 and 7 is provided by a pipe 16 and pump 17 and by a pipe 18 and pump 19 respectively.

Sulphur dioxide relieved from the digester at pressures from 15 pounds per square inch to 0 is delivered to the vessel 8 through the pipe 12, where it is met by circulating liquor delivered by pump 24 through pipe 25. Also, any sulphur dioxide which is not absorbed in the vessel 7 passes through the pipe 20 into the vessel 8, from which the weak liquor is delivered by a pump 21 and pipe 22 into the vessel 7. Finally, the vessel 9 affords storage for the weak bisulphite liquor produced as hereinafter described. This liquor is delivered through pipe 23 to the vessel 8 as required. The liquor passes successively through the vessels 7 and 6 respectively as hereinbefore indicated, where it absorbs more sulphur dioxide until it reaches the ultimate strength required for cooking liquor and is introduced into the digester 5 through a pipe 26.

Although the digester may be operated as in the customary cooking operation, it is preferred to use the low liquor ratio as described in the patent to George V. Palmrose, No. 2,192,239 issued March 5, 1940, and provision is made, therefore, for circulation of the liquor through a pump 27 and pipe 28 to a heat exchanger 29 wherein the liquor may be heated by means of steam or otherwise, and thence through a pipe 30 into the digester.

At the conclusion of the cooking operation, the free sulphur dioxide is relieved and delivered as hereinbefore described into vessel 8. The contents of the digester, including the pulp and the acid waste liquor, are then delivered by a pump 31 and pipe 32 into a tank 33 from which any remaining gases, including steam, escape through a pipe 34. The pulp and the waste liquor is delivered by a pump 35 and pipe 36 to a series of filter washers 37. For convenience, only the last washer of the series is illustrated. It is supplied with wash water through the pipe 38. The pulp is withdrawn from a launder 39. The waste liquor escapes through a pipe 40 to a tank 41. It will be understood that in the filter washers pulp advances counter-current to the travel of the washing liquid, being finally washed with fresh water, the wash liquid traveling through the series of washers and combining with the waste liquor which accumulates in the tank 41.

The waste liquor is delivered by a pump 42 and pipe 43 to a scrubbing tower 44 through

which it is circulated by a pump 45 and pipe 46 which delivers the liquid in sprays 47. The liquor is then withdrawn through the pump 45 and pipe 48 and delivered to a bank of multiple effect evaporators 49. The liquor is circulated through the successive elements of the bank of evaporators by pipes 50 and pumps 51 counter-current to the vapors which travel through pipes 52. A heating agent such as steam is introduced through a pipe 53, and the vapors escape through a pipe 54 to a condenser 55 where, as hereinbefore indicated, water is condensed from the vapors, leaving sulphur dioxide which is delivered through a pipe 56. The condensed water passes through a pipe 57 to a sump 58. The sulphur dioxide, substantially free from water vapor, passes from the pipe 56 into a jet condenser 59 where it is mingled with magnesium bisulphite liquor produced as hereinafter described and accumulated in the tank 60 whence it is circulated through the pump 61, pipe 62, heat exchanger 63 and pipe 64 to the jet condenser 59. Thus, the sulphur dioxide relieved from the evaporating system is recovered as free sulphur dioxide absorbed in the magnesium sulphite liquor which may be delivered through the pump 61 and pipe 65 to the vessel 9 where it affords the basis for the cooking liquor being already fortified in free sulphur dioxide and absorbing in the vessels 8, 7 and 6, respectively, additional quantities of sulphur dioxide, to produce the strong cooking liquor.

Alternatively, the sulphur dioxide from the condenser 55 may be drawn through a reciprocating vacuum pump 93 which will compress the gas to the required pressure to permit delivery thereof through the pipe 94 to one of the vessels 6 or 7 as may be desired. In that case, the liquor from the tank 60 will pass directly to the vessel 9.

The concentrated waste sulphite liquor from the evaporation system is delivered through a pump 66 and pipe 67 to a furnace 68 where it is burned with air supplied through a pipe 69 and blower 70. Magnesium compounds and sulphur may be introduced at this point if needed to make up losses. The air may be preheated in a heat exchanger 71 by products of combustion delivered from the furnace by the pipe 72. The air is supplied through a pipe 73 and is delivered to the blower by a pipe 74.

Combustion of the liquor in the furnace results in a pulverulent ash of magnesium oxide. The heat generated by combustion may be converted into steam in a boiler 75, and the steam may be withdrawn through a pipe 76 and utilized for any desired purpose, as for example in the evaporating system or elsewhere in the plant.

The hot combustion gases carrying the bulk of the finely divided magnesium oxide ash are delivered through a pipe 77 and blower 78 into a dust catcher 79 from which the gases escape and are delivered through a blower 80 and pipe 81 to the scrubbing tower 44 previously described. The magnesium oxide ash is delivered to a tank 82 and supplied with water through a pipe 83 which converts it into a slurry. This slurry is delivered through a pipe 84 to a tank 85 whence it is delivered by pump 86 and pipe 87 to a packed absorption tower 88. In this tower the slurry is subjected to the cool furnace gases containing sulphur dioxide derived from the combustion of the waste liquor. These gases are delivered from the scrubbing tower 44 to the packed absorption tower 88 by a pipe 89. The sulphur dioxide in the

gases is combined with the magnesium oxide in the slurry to produce magnesium bisulphite which is withdrawn through the pipe 90 and delivered to the tank 60. The balance of the furnace gases escapes through a pipe 91 substantially free from sulphur dioxide. Circulation of the slurry during the absorption operation is permitted by a pipe connection 92 to the tank 85. An additional absorption tower, similar to the tower 88, may be utilized, if desired, to facilitate recovery of the sulphur dioxide in the furnace gases.

As will be seen from the foregoing description, the operation affords a complete cycle in which strong cooking liquor, fortified with the necessary amount of free sulphur dioxide, is produced continuously for use in the digester. The sulphur dioxide relieved from the digester and sulphur dioxide recovered during evaporation of the waste liquor and by the subsequent combustion thereof, are utilized to produce and to fortify the magnesium bisulphite liquor, affording fresh quantities of the liquor without necessary additions from other sources. There are no waste products to be discharged. Losses, if any, can be made up by the addition of sulphur dioxide from other sources and of the base metal as may be required. In general, however, the free sulphur dioxide operates in a cycle in which it performs its function in the digester and is recovered and reutilized in the preparation of fresh cooking liquor.

The magnesia which is the metallic base necessary in the process is similarly recovered and travels in a cycle in which it is combined with sulphur dioxide to produce cooking liquor. The organic material, freed from sulphur, is burned, and the heat of combustion is utilized to produce steam employed in the operation. Thus, the efficiency of the process is maintained, and uneconomic factors are eliminated, including the discharge of waste products to rivers and streams and to the atmosphere.

Various changes may be made in the form and construction and operation of the apparatus, and in the details of procedure, without departing from the invention or sacrificing any of the advantages thereof.

We claim:

1. A cyclic method of treating ligno-cellulosic material which comprises the essential steps of cooking the ligno-cellulosic material under pressure with a solution of magnesium bisulphite containing a substantial excess of free sulphur dioxide, releasing gases during and after the cooking, separating the acid waste liquor from the treated cellulosic material after completion of the cooking operation, evaporating and burning the separated acid waste liquor to produce an ash consisting mainly of magnesium oxide and combustion gases containing sulphur dioxide, adding magnesium compounds and sulphur as required to make up losses of the evaporated liquor during the burning of the waste liquor, making a slurry of the magnesium oxide ash, absorbing the sulphur dioxide in said combustion gases in said slurry to reform magnesium bisulphite to be used in a subsequent cooking operation, condensing the vapor resulting from the evaporation of the waste liquor to separate sulphur dioxide therefrom, absorbing the separated sulphur dioxide in the magnesium bisulphite liquor produced from the ash and the sulphur dioxide of the combustion gases, and returning the reformed magnesium bisulphite

containing the absorbed sulphur dioxide for further cooking of ligno-cellulosic material.

2. A cyclic method of treating ligno-cellulosic material which comprises the essential steps of cooking the ligno-cellulosic material under pressure with a solution of magnesium bisulphite containing a substantial excess of free sulphur dioxide, releasing gases during and after the cooking, separating the acid waste liquor from the treated cellulosic material after completion of the cooking operation, evaporating and burning the separated acid waste liquor to produce an ash consisting mainly of magnesium oxide and combustion gases containing sulphur dioxide, adding magnesium compounds and sulphur as required to make up losses of the evaporated liquor during the burning of the waste liquor, making a slurry of the magnesium oxide

5 ash, absorbing the sulphur dioxide in said combustion gases in said slurry to reform magnesium bisulphite to be used in a subsequent cooking operation, condensing the vapor resulting from the evaporation of the waste liquor to separate sulphur dioxide therefrom, absorbing the separated sulphur dioxide in the magnesium bisulphite liquor produced from the ash and the sulphur dioxide of the combustion gases, thereafter fortifying the reformed magnesium bisulphite liquor with sulphur dioxide relieved from the digester at low pressure and thereafter at higher pressure, and returning the reformed magnesium bisulphite liquor containing the absorbed sulphur dioxide for further cooking of ligno-cellulosic material.

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