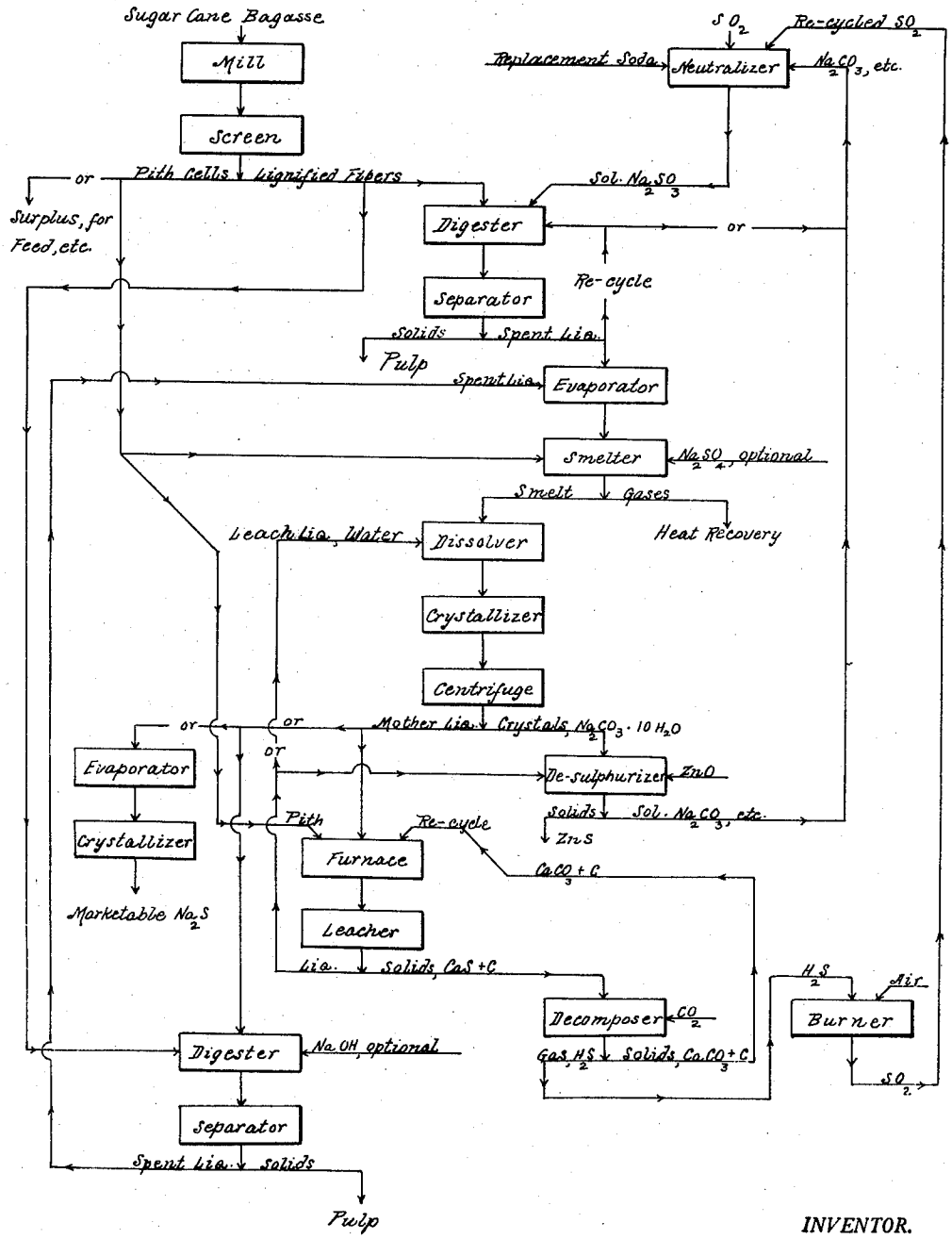
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METHOD OF MAKING PAPER PULP

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METHOD OF MAKING PAPER PULP

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The object of my invention is particularly the production of a good and useful sheet of paper from the residue left after expressing, or otherwise extracting, the sugar-bearing juice of sugar cane, generally referred to under the name of "bagasse." However, as many woods now used in making paper pulp can also be treated in this manner with a somewhat higher pulp yield than standard practice, I take the broader view and, specifically, I do not limit my process to the sugar cane field.

I shall, therefore, first give a concise description of my process, as applied to bagasse, and at a later period I shall show how the underlying technique can advantageously be applied in many a kraft and/or sulphate mill. I also wish to state that though I believe the instant application to be not only useful but also new, yet the underlying chemistry is very old. I shall draw freely upon three United States patents, all now expired, which were granted to me many years ago. These patents are: No. 1,823,519, issued September 15, 1931; No. 1,902,106, issued March 21, 1933; and No. 2,031,239, issued February 18, 1936.

At the time these patents were issued to me the underlying chemical reactions were as well known as they are today. In the instant application I use the same chemical reactions that are contained in said previous patents, but the purpose is radically different. In the oldest patent I dealt entirely with the orthodox sulphite operation. In the second patent I used the same chemical step for the purpose of making it possible to cook, on a cyclic basis, with sodium sulphide as the pulping agent, but such use of sodium sulphide had been patented at least 50 years before. In the third patent, I disclosed how both could advantageously be used on bagasse using two distinct cooking methods.

In the method I now disclose I deal with what is generally called the "neutral sulphite" pulping method. Although this suggests the orthodox sulphite method, the similarity is only of language. In the "orthodox" or acid sulphite cook the actual pulping agent is "free" sulphur dioxide, the cook being a highly acid process. The function served by the sulphite is to combine with the products of the hydrolysis produced by said "free" sulphur dioxide. In the "neutral sulphite" process we deal with a true solution of the non-cellulose ingredients in sodium sulphite directly, i.e., delignification depends entirely upon the action of sodium sulphite as it is the sole active agent present therein. Consequently, it is necessary in this process to use at least 5 times the amount of sodium sulphite that would be needed if the acid cook were made with "free' sulphur dioxide. Such cooking with a very large amount of sodium sulphite is well known and it is very much desired for unlike the customary yield of pulp of about 45% in standard processes this method of working with the neutral sulphite gives as high as 65% of pulp, very little cellulose being hydrolysed to soluble forms.

The large quantity of neutral sulphite needed, combined with the fact that a satisfactory method has not yet been devised whereby the soda may be recovered and

returned to the cooking step, limits the use of this interesting pulping operation to the amount that can be combined with a kraft cook in which the salt cake is replaced by the spent cooking liquor from the neutral sulphite pulping. Inasmuch as today's demand for nuisance abatement has led to extensive use of Cottrell precipitation, and other ways of reclaiming fume, the amount of salt cake going into a kraft mill is now but a fraction of what it was in the past and thus the amount of neutral pulping that can be introduced becomes small indeed.

Of course, in all these cases, if the spent liquor be "smelted" in the standard fashion, then the solution of such "smelt" will consist essentially of the carbonate and sulphide of soda with a little sulphate and miscellaneous soda salts. The difference consists solely in the respective amounts of carbonate and sulphide produced by the entirely different types of liquor resulting from the various processes. Now the salient feature of the recovery system which I developed and disclosed in the three patents previously referred to consisted of employing crystallization as the means of separating from one another the carbonate and sulphide of soda resident in such a solution of "smelt" which is universally referred to in the vernacular of pulping as "green liquor," the spent liquor being called "black" and the new, regenerated liquor being called "white." Of course, there is no new discovery in such a separation, any table of solubilities of soda salts shows the relation plainly. Nevertheless, the application of this step to green liquor was new, and hence its inclusion in both an acid and an alkaline cook, respectively, conveyed patentability.

In spite of the similarity of name, as already referred to, "neutral sulphite" cooking differs more from "acid sulphite" and from any form of "alkaline" cooking than these two versions do from one another. Consider only the character of the pulp produced and the inference becomes obvious. If the same wood species be pulped with caustic soda alone; or with a mixture of caustic and sulphide (kraft); or with sulphide alone; or with acid sulphite cooking (orthodox sulphite); and if the resultant pulp be then bleached it is often impossible to differentiate between the processes employed, the character of the pulp being identical, consisting essentially of alpha-cellulose.

Contrariwise, in neutral sulphite cooking a great deal of beta- and gamma-cellulose resident in the wood remains undissolved and the high pulp yield is due largely to the preservation of such fiber constituents as an integral part of the final pulp. Obviously, the character of the resultant spent cooking liquor must be entirely diverse from that produced by any of the older forms of pulping.

I have already mentioned that the fibrous part of the sugar cane is particularly suitable to pulping with neutral sulphite. By orthodox processes the yield of pulp is low and the resultant pulp is weak. The best and strongest pulp is produced by using a "sulphate cook with 100% sulphidity," or in other words by cooking with sodium sulphide in accordance with my expired Patent No. 1,902,106, but still the yield is low. On the other hand, the use of the neutral cook is excellent. The yield is high, the pulp is good, and both time and sulphite usage are less than any wood with which I am acquainted. These advantages are due in part to the chemical composition of the cane fiber and in part to the physical condition inseparable from its origin, milling, and final preparation.

This final preparation consists in removing substantially all the pith cells that form about one-third of the total bagasse. I do this by subjecting said bagasse to attrition in a device which in my drawing I have simply called a "mill." This drawing will first be briefly described as follows: Prepared bagasse is divided into two parts, one part being cooked with neutral sulphite, another part with the mother liquor, from a subsequent crystalliza-

tion, consisting essentially of sodium sulphide. The combined spent cooking liquors are commingled in the evaporator on their way to the smelter. The smelt is dissolved in water and separated by crystallization into crystallized sodium carbonate and said sulphide-rich mother liquor. Two alternate methods of treating said sulphide mother liquor are also disclosed namely; direct sale, and the conversion of said sulphide to carbonate by the use of the old Leblanc soda process. In the latter case, by-product calcium sulphide is decomposed by carbon dioxide to liberate hydrogen sulphide. The actual chemistry involved throughout was old a century ago, nevertheless it had been made a part of many recent patents. From now on, my process in its preferred form is best followed on said drawing and I shall confine myself chiefly to said steps with only an interpolation, now and then, relating to my process when carried out on wood.

This milling is preferably done wet and the mill may take the form of a tube mill containing a shallow layer of pebbles. After milling, at a rate determined by the feed, the fiber has been liberated from adherent pith cells and separation is made by screening on, say, a 20 mesh screen, the pith cells passing through and the fibrous part being retained. Owing to the diversity of cane species and to different forms of milling practice no specific ratios of time, pebble weight, water volume, etc. can be prescribed but the operator will have do difficulty in obtaining a good product by varying said items in accordance with the results obtained.

The cleaned lignified fiber is now cooked in a "digester" with a solution of the neutral sulphite of sodium a provisional allowance in starting being 40% or more on the bone dry weight of crude product. Again, time, temperature, and concentration of cooking liquor are ultimately adjusted in accordance with the specific limitations imposed by the character of the raw material and with the requirements of the finished product. I have shown the cooking liquor as made in a "neutralizer" by the interaction of re-cycled sulphur dioxide and sodium carbonate supplemented by such amounts of these items as have been consumed in the over-all operation.

After cooking is finished the fiber is next separated from the spent cooking liquor and any further processing of said fiber is outside of this disclosure. I have shown a part of this separated liquor as returned to the cooking cycle either by commingling with cooking liquor in the digester or in the neutralizer at the option of and in the amount desired by the operator. Naturally, the more recycling practiced the less becomes the burden upon the evaporator which is the next step on the drawing.

After evaporation comes the smelting step which is in accordance with standard practice in sulphate cooking. I have shown a commingling with a part of the separated pith of the cane in the event that additional fuel be needed in the smelter to balance the higher soda-organics ratio in the cooking liquor. If wood be considered, where obviously there is no pith and no pith reject, any deficiency in organics can be met by adding discarded bark, sawdust, wood waste, etc. of which there generally is a surplus anyway at a mill.

The smelt is then dissolved in water as usual and forms a "green liquor" consisting essentially of carbonate and sulphide of soda but with much more sulphide than in customary practice. If the concentration be kept high, by regulating the water input into the dissolver, only cooling is needed to produce a crop of crystals of the decahydrate of sodium carbonate. Said crystals will contain but little sulphide, if the concentration be correct, and as the actual ratio of sulphide to carbonate depends upon too many factors for prediction, said concentration must be established by smelter practice and adjustment in gravity made to the point where but little sulphide is retained in the crystal product.

Manifestly any conventional method may be used to separate the crystals from the mother liquor, but I prefer the centrifuge because of the thorough purging from the high-sulphide mother liquor thus attained. In most cases this sodium carbonate is pure enough to use forthwith in making up fresh cooking liquor but it is unavoidable that any sulphide retained therein thus becomes converted into the thiosulphate. It has been well demonstrated that it takes but little of said thiosulphate to injure the neutral sulphite cook so where the best results are wanted it will pay to desulphurize the sodium carbonate before it is contacted with the sulphur dioxide.

How this may be done I have indicated on the drawing as an intermediate step between the centrifuge and making the regenerated cooking liquor. In the "desulphurizer" I have shown zinc oxide as an addition to a solution of the crystals with zinc sulphide being separated thereafter. It is advantageous to bring the solution up to the boiling point during the treatment. It is, of course, axiomatic that roasting will regenerate the zinc sulphide and the sulphur dioxide thus produced can likewise be used in making fresh cooking liquor. These obvious steps I have not indicated on the drawing.

While I consider this method of desulphurizing the best and simplest there is another approach which may be substituted. It is possible to remove the thio-sulphate from the cooking liquor by the cautious addition of a heavy metal salt, such as the sulphates of copper or zinc or soluble forms of lead. From such material thiosulphate will precipitate the corresponding heavy metal sulphide and the cooking liquor thus becomes desulphurized. It is, of course, quite impossible to designate all such possible variations on the drawing so it has been intentionally omitted.

Referring now again to the drawing, I have shown the high-sulphide mother liquor discharged from the centrifuge as split into three separate streams. Any one of these may be used, or a combination of any two, or a combination of all three versions, at the will of the operator. I will first take the line to the right, then the intermediate one, and finally I will describe the one to the left.

I have shown the liquor as entering a furnace, which by preference is some type of a revolving kiln. It is here commingled with a recycled mixture of calcium carbonate and carbon, from a subsequent step, and with some of the pith cells from the purification of the bagasse. The atmosphere of the furnace and the presence of free carbon in the charge assure a reducing fusion though actual reduction is not called for but it is desired to prevent the re-oxidation of sulphide to sulphate which otherwise might take place. As only fusion is called for the operation is rapid and bears no resemblance to the old Leblanc soda process from which it might appear to have been derived. In this historic process much sulphate is reduced with consequent high heat demand, much excess of carbon is mandatory as is a large excess of limestone which in the furnace becomes converted to calcium oxide. All these items are absent in the present case. The only similarity resides in the result which consists of a migration of the sulphur from the soda salt to the lime combination, remaining, however as a sulphide. In the subsequent step, in the leacher, water is used to remove the soluble soda salts from the insoluble lime salt, calcium sulphide. The soda salt, chiefly carbonate, still retains an appreciable amount of sodium sulphide, due to incomplete reaction but this is no more than can easily be dealt with in the de-sulphurizer, to which I have indicated it sent.

I have also shown an alternate destination for said leach liquor which can be used in the event that the sulphide content rises too high to deal with in said de-sulphurizer, namely, to return it to the smelt dissolver. I have indicated this step on the drawing. Manifestly if this be done then sodium carbonate, with little inherent sulphide, is split off in the crystallizer while the resident sulphide is recycled once more to the fusion with calcium carbonate and resultant conversion to sodium carbonate.

It is the aim and object of this alternative step to reduce as much as possible the de-sulphurization with zinc oxide, for while this is a well known step and entirely operative it has much mechanical difficulty as well and thus is reasonably expensive. Its use should be restricted to the absolutely essential needs of the operation.

In any event I have now disposed of the sulphide produced in the smelting step and only pure sodium carbonate is cyclically returned to the making of fresh cooking liquor. The solids, separated in the leaching step and consisting essentially of calcium sulphide and residual carbon next requires attention for merely discarding it is not to be thought of. I have indicated it treated with carbon dioxide in a "decomposer" which is merely an agitated tank with a good gas distribution for the entering carbon dioxide. This may be simply chimney gas but better still the flue gas from the furnace in which the calcium sulphide originated, such gas being rather high in carbon dioxide. Evolution of hydrogen sulphide which result is burned to sulphur dioxide and recycled to the initial making of neutral sulphite cooking liquor. Calcium carbonate and residual carbon remain behind and these are shown as re-cycled once more to the furnace step. The composite of these steps thus constitutes a recovery system for neutral sulphite cooking.

I will now return to the second method of disposal of the high sulphide liquor as discharged from the centrifuge, the intermediate line before referred to. Disposal in this instance consists of using it as a cooking liquor for an additional amount of clean bagasse. I have indicated this as taking place in a "digester" of standard construction for alkaline cooking. Pulp and liquor are separated from one another in a "separator" of any type and while the pulp produced is not identical with the former type the mixture will nevertheless give an acceptable sheet and in many instances will be preferred.

The liquor from said cooking step is then shown as recycled to the evaporator which in turn feeds the smelter. Some of the sulphur, resident in the sulphide cooking liquor is eliminated in the cooking itself as volatile sulphur compounds. Another portion is driven off in the carbonizing which takes place in the top of the smelter before smelting, proper, commences. All such sulphur elimination liberates the corresponding amount of soda so the cooking and smelting step combined serves the same purpose as the previously described operation, giving as its ultimate product more sodium carbonate to use in making neutral sulphite cooking liquor.

It is obvious that the two steps just described can be combined to any extent desired thus permitting any relative production of the two types of pulp. I have shown as optional the addition of caustic soda to the last named digester, thus converting this sulphide cooking into any modification of conventional kraft cooking that may be desired. Of course, such caustic soda would, in practice, by made by causticizing a part of the recovered carbonate. I have thus shown an integrated system of neutral sulphite cooking with the graft cycle in which any desired amount of the total pulp can be neutral sulphite.

I will now describe the third version of the utilization of the high sulphide liquor, the one that occupies the extreme left hand position. It is based upon the fact that sodium sulphide is a relatively expensive chemical, at least when compared with the price of soda ash and salt cake. It is, therefore, an economic advantage to use said high sulphide liquor as a source of marketable sodium sulphide. To achieve this objective I have shown a further evaporation followed by crystallization. Sodium sulphide crystals are about two-thirds water and when melted in its own water of crystallization, slightly evaporated and settled, the supernatant fusion can be flaked at once for 60% or "concentrated" sulphide. The only objection to this plan, which is quite profitable, is the limiting size of the sodium sulphide market which probably is not much above 60,000 tons per annum. To the extent, however, that it can be employed it furnishes the most lucrative version of my method for making neutral sulphite.

Naturally, there are many possible variations of the theme as herein disclosed. As I have already implied the solution of smelt could be converted into a mixture of sodium carbonate and caustic soda if it were but boiled with enough zinc oxide to bring this about, but such conversion is far more expensive and difficult than the one I have described. Nevertheless it could be used. So, likewise, in the kraft process the steps I have herein disclosed can be used to control the "sulphidity" of the operation. Manifestly, the withdrawal of some sodium carbonate by crystallization from the green liquor will increase the percentage of sulphide in the remainder. Likewise, the conversion of a part of said sulphide into caustic soda and/or sodium carbonate will result in a decrease in the resident sulphide.

Inasmuch as a kraft cook is essentially the work of caustic soda only modified by the presence of a minor amount of sodium sulphide, it would be possible to work on white liquor instead of green and achieve the same overall result. Thus in an integrated system of neutral sulphite and kraft cooking wherein the spent liquor of the neutral cook is commingled with the black liquor from a kraft cook before smelting the final white liquor could be processed as follows: A portion of said white liquor could be completely desulphurized with zinc oxide and afterwards be neutralized with sulphur dioxide to make a faultless cooking liquor for the neutral sulphide cook. If this procedure still leaves too much sulphide in the kraft liquor then a larger portion could be desulphurized and after satisfying the requirements of the neutral cook the balance could be returned as a sulphur-free caustic liquor to the kraft cooking cycle. Another way of achieving this would be to crystallize out of the caustic white liquor such sodium sulphide as desired and then process said sulphide by itself as herein described thus leaving but little sulphur to take out with zinc oxide in that fraction used to make neutral sulphite cooking liquor. Finally, the entire green liquor could be furnaced with calcium carbonate without the prior removal of carbonate. It would mean dragging a great deal of inert carbonate through many steps and would thus cost more both in plant and in operation but it would be operative. While all such expedients could be used they would represent rather a way of avoiding the specific claims of this application than serving any useful purpose. In the main, I believe that the best and cheapest way of solving the regenerative phases of a neutral cook resides in following my herein described preferred version, be the raw material bagasse or conventional pulping wood species.

One final notation on the drawing requires comment. I have shown an optional addition of salt cake at the smelter as a means of furnishing not only the needed soda but also sulphur. In all such integrated systems, with or without the marketing of sulphide, the cheapest source of both will doubtless be salt cake. All such items as well as the many variations rendered possible by this disclosure I consider as being within its framework.

Having thus fully described my process, I claim:

1. The method of making pulp from sugar cane bagasse which comprises; separating pith cells in said bagasse from the resident lignified fibers by subjecting same to attrition to liberate the pith cells from their adherence to the fibers and to one another and subsequently removing said pith cells by screening; digesting the cleaned fibers in a solution of neutral sodium sulphite until the resident cellulose is substantially freed from encrustants, said sodium sulphite being the sole active agent involved in removing said encrustants; separating the cellulose from the spent cooking liquor; incinerating said spent liquor; dissolving the resultant smelt in a solution of sodium carbonate obtained in a later step of the process; crystal-

lizing a part of the therein resident sodium carbonate; separating said crystallized carbonate from the residual sulphide-containing mother liquor; neutralizing the separated crystallized carbonate with sulphur dioxide to make fresh cooking liquor; commingling the mother liquor previously referred to with calcium carbonate and then drying and fusing the mixture; leaching the resultant fused product with water to obtain a solution of sodium carbonate and leaving a residue of calcium sulphide; recycling said solution of sodium carbonate as the dissolving medium for smelt where previously called for.

2. The method of making a neutral sulphite pulp from sugar cane bagasse set forth in claim 1, with the added step that the crystallized sodium carbonate obtained therein be purified from sulphide contamination prior to neutralization with sulphur dioxide, said purification consisting in heating with zinc oxide and separating the zinc sulphide thus produced.

3. The method of making a neutral sulphite pulp from sugar cane bagasse set forth in claim 1, with the added step that a portion of the pith separated from the lignified fiber be commingled with the mixture of mother liquor and calcium carbonate described therein before said mixture is subjected to fusion, thus largely inhibiting oxidation during said fusion.

4. The method of making a neutral sulphite pulp which comprises; digesting lignified cellulose with a solution of sodium sulphite, said sodium sulphite being the sole active agent in said delignification, until the resident fibers have been liberated; separating said fibres from the spent cooking liquor; incinerating said spent liquor; dissolving the resultant smelt in a solution of sodium carbonate obtained in a later step of the process; crystallizing the resultant solution thus obtaining in crystal form principally the therein resident sodium carbonate and a mother liquor containing essentially the resident sulphides; separating said crystals of carbonate from said mother liquor; neutralizing said separated crystal sodium carbonate with sulphur dioxide to constitute fresh cooking liquor; commingling the mother liquor previously referred to with calcium carbonate and then drying and fusing the mixture; leaching the resultant fused product with water to obtain a solution containing principally sodium carbonate and an insoluble residue of calcium sulphide; and re-cycling said solution of sodium carbonate to dissolve smelt where previously called for.

5. The method of making a neutral sulphite pulp set forth in claim 4, with the added step that the crystallized sodium carbonate obtained therein be purified from sulphide contamination prior to neutralization with sulphur dioxide, said purification consisting in heating with zinc oxide and separating the zinc sulphide thus produced.

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