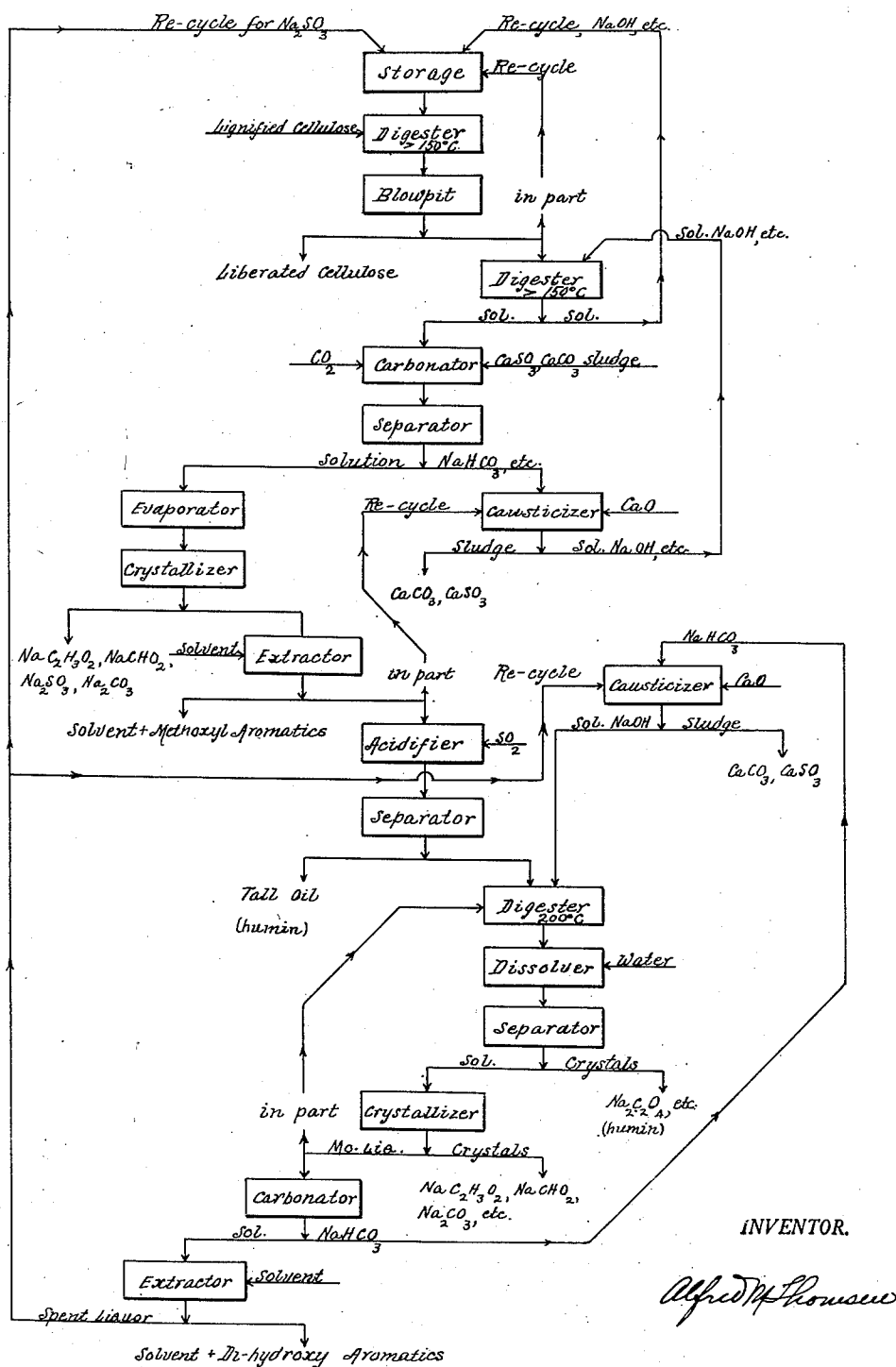


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**METHOD OF COMPLETELY RESOLVING
LIGNIFIED CELLULOSE**

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3 Claims. (Cl. 260—527)

This application is a continuation, in part, of Ser. No. 771,793, issuing under date of Nov. 18, 1952 as U. S. Patent No. 2,618,610. It is also a continuation, in part, of Serial No. 257,294, filed Nov. 20, 1951 under the title, "Extracting Aromatic Compounds from a Lignin-Cellulose Complex."

In the former of these applications I have dealt with the subject of degrading a cellulose-lignin complex under the general aspect of pulp making. Remaining within conventional limits as to time, temperature, and alkali concentration that pertain to the making of paper pulp of high strength and good bleachability I have shown that by an involved system of the recycling of residuals it is possible to achieve a notable liberation of the aromatic nucleus, resident in or formed from lignin, concentrated in a definite fraction of the spent cooking liquor. I have then shown the extraction of said aromatics and the recovery by a special type of incineration of the alkali metal compound employed in cooking and its conversion into a form suitable for the digestion of the cellulose-lignin complex serving as raw material for the process. In the latter application I have disclosed the additional effect of increasing the alkali ratio and the temperature in the subsequent treatment of the spent liquor after cooking, thus obtaining a greater yield.

I have further disclosed the recovery of notable amounts of organic acids, liberated or formed in the attack upon the complex or its constituents, as well as the aromatic nucleus itself. Final disposal of the organics not extracted and of the alkali metal not re-cycled is the heating of a carbonized residue in nitrogen thus forming an alkali metal cyanide.

In the instant application I have further developed this theme in such a manner that the aromatic nucleus is recovered partly in its methoxyl form and partly in its dihydroxy form. Simultaneously the acetyl component of the complex is very fully liberated and recovered as are fats and carbohydrates of the non-cellulose class, after conversion to organic acids. The simplest way to explain my process is to follow the "preferred version" which I have illustrated in the accompanying flowsheet. Of course, I do not confine myself exclusively to the steps as set forth therein nor to the specific sequence in which the various steps are performed as much will depend upon the types of lignified cellulose selected for the operation. In general, the following facts apply.

It is of no particular moment to consider whether the final end products recovered are actually present in the lignified complex or whether they are produced in the step undertaken to put them in proper form for recovery. It suffices to say that the very method of liberation is also to a certain extent destructive to the substances formed. Actual recovery is thus a compromise between liberation and recovery. Prolonged digestion to secure a higher yield is thus ultimately voided in effect by the decomposition of the substance or substances that have been produced. Optimum results can only be secured

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through empirical observation. Also, while this disclosure appears limited to a caustic cook modified with sulphite, my process could be used directly upon the spent cooking liquor of the orthodox soda, sulphate, sulphite, or kraft pulp mill operation.

The term "lignified cellulose" as used herein is any combination of lignin and cellulose in the form in which nature has produced it. Such combinations are never pure but contain a most variable mixture of carbohydrates, such as pentoses and poly-saccharides, fats, waxes, resins, sugars and so forth. I overcome the difficulty of decomposition by never attempting to secure a complete conversion at a single stage, instead I operate in a series of stages with continual re-cycling of incomplete reaction products. In this manner little, if any, organic matters require to be removed by incineration such as I have employed in my previous disclosures. In the event that an accumulation of impurities should occur then, manifestly, a small fraction of the re-cycled products can be split off to an incineration step which may be effected in any conventional manner as its economic value will be very small.

On the flow sheet I have represented a storage tank for cooking liquor followed by an orthodox pulp digester for the cooking step. I have indicated that said digester be used at temperatures below 150° C. as higher temperatures produce some decomposition of the aromatic nucleus in its methoxyl combination. The digester is discharged to the blowpit where separation is made between the fibrous cellulose and the dissolved portions of the complex. As large a fraction as possible of the spent cooking liquor is recycled to the storage tank. It should not be less than 50% of the total and may well be much larger. In this manner a very concentrated liquor is obtained for the next step which again is termed a "digester." The temperature is again placed as below 150° C. and for the same reason as previously given but the concentration of caustic alkali is raised to such an extent that three times as much caustic is present than total organic matter in the liquid.

The actual time of digestion cannot be given as it will vary with whatever type of lignified cellulose is under treatment. Provisionally it may be placed at 6 hours and the time will then be varied according to the actual recovery of methoxyl aromatics subsequently obtained. Similarly, no time or concentration is given for the first digestion as this will be represented by orthodox pulp experience and the chemical and physical characteristics of the pulp yielded thereby.

After completion of the desired time the digester is emptied of its contents and this is divided into two portions. One portion is re-cycled to "storage" to furnish the caustic increment for the first digestion. Naturally, much sulphite will accompany it as well. The actual percentage will be determined by the rise and fall in caustic of the contents of the storage tank. The remainder, not thus recycled, is sent to the "carbonator" where it is completely saturated with CO₂ thus providing maximum removal of soda salts as the bicarbonate. An addition of a sludge of mixed CaSO₃ and CaCO₃ is indicated. Such sludge is obtained in a subsequent step and a part of the sulphur otherwise lost in said sludge may thus be saved. Its amount depends, of course, on the amount of sulphite in the storage tank, which provisionally is placed at from 50% to 100% of the caustic content, but may be widely varied.

After complete carbonation the charge is filtered or centrifuged in the "separator" and the resultant crystal product is causticized in the "causticizer" by the addition of lime in the conventional manner. Whatever organic matter is co-precipitated by the CO₂ treatment is thus once more put back in solution in the causticizing operation

and recycled to the first of the "caustic" digesters, as separate from the "pulp" digester where the chemical operation started.

The liquid portion from the "separator" is then sent to an evaporator for further concentration and to a "crystallizer" which yields a crystal product and a mother liquor. The crystal product is a mixture of acetate, formate, carbonate and sulphite of the alkali metal employed, soda alone being indicated in the drawing but potash could manifestly be substituted. Inasmuch as the soda salts of acetic and formic acid are far more soluble than the corresponding carbonate and sulphite it follows that separation is readily made between these groups, the former being further processed for the contained acids, the latter re-cycled to the operation where called for. Such procedure, being entirely conventional, is not shown but the application is obvious.

The mother liquor from the crystallizer next passes to an "extractor" where it is treated with any desired solvent, substantially immiscible with water, for the aromatics involved. The greatest latitude may be used, common ether, higher alcohols, benzene and chlorinated solvents being all admissible. The choice is a matter of preference with the operator. Such extraction is never complete but this is of little moment in my process while often it is the dominant factor stressed in many an issued patent.

The reason for this anomaly is simple. The major part of the extracted solution is re-cycled as the needed fluid in the causticizing operation previously described, only a minor part being sent to the succeeding step. In the part re-cycled said aromatics are at once converted to soda salts where they are virtually immune from decomposition at the low temperature employed. In addition, the unresolved lignin derivatives are once more subjected to the action of caustic and thus ultimately almost all possible fractions of the aromatic family are recovered by further solvent extractions.

That portion of the extracted liquor not re-cycled is then sent to an "acidifier." Any mineral acid may be used but only SO_2 is indicated on the drawing. By means of a "separator" a tall oil product is then removed. This may be by plain settling or by the use of a centrifuge. If an appropriate solvent be likewise added then much aromatic material will likewise become a component of the separated fraction. That is as the operator selects and forms no particular part of this disclosure. Manifestly, those aromatics that form addition compounds with sodium bisulphite remain in solution and are ultimately obtained, at least in part, by subsequent re-cycling.

After the tall oil separation the remaining solution is again treated in a "digester" with added caustic from another "causticizer." The temperature is indicated as 200°C . but this may be varied by as much as 30°C ., up or down, if compensation is made by increased caustic or increased time if the temperature be lowered. In the reverse direction, manifestly, such items would be decreased instead. Provisionally, a 6 hour period may be used and this can then be altered to suit the actual effect obtained. Ratio of caustic to organics should be about the same as in the previous caustic digestion, approximately 3:1.

Inasmuch as the pressures required to reach the temperatures involved are rather high it is in general more convenient to reach such temperatures by permitting the escape of steam until the water content is so reduced that the melting point of the "mix" shall be at the required limit. A closed vessel, to avoid oxidation, but operating under normal pressure is thus a satisfactory type of "digester" for this step. Subsequently said mix is commingled with sufficient water to make it mobile, in the dissolver and then separated into a liquid and a solid portion in the subsequent "separator." Using a mini-

mum of water the solids are chiefly sodium oxalate and humin.

On cooling the resultant solution a copious crystallization will be obtained consisting of the same components but in different proportion to that previously described. A little oxalate will also be present. The same technique of separation can be used with the same disposal of products.

In the drawing I have indicated a re-cycling of a part of the mother liquor to the digester but this is optional. The remainder, or the total amount if there be no re-cycling, is then carbonated, the bi-carbonate separated and causticized for re-use. The resultant solution now passes to another "extractor" where solvent is used in the same manner as heretofore described. The spent liquor, after such extraction, is re-cycled in its entirety, in part to the second causticizer and in part to the head storage tank of the entire system. There is thus no provision for any waste save the humin fractions obtained at sundry points. Obviously, if these will show adequate results on further caustic digestion they would in turn be re-cycled to the causticizers.

The over-all result of my process is thus seen to be a separated type of cellulose, organic acids, fats and resins, and sundry aromatic compounds corresponding in general to the benzene ring with additions of hydroxyl and methoxyl. High yield is based upon the recovery of liberated products at sundry points with systematic re-cycling of all the unused fractions until complete resolution with a minimum of destruction has been attained. The principal source of elimination of carbon from the system, apart from that represented in finished products, is in the form of CO_2 which not only appears in the large amounts of carbonate produced but is even evolved in considerable amount from the second, high temperature, caustic digestion. Losses of soda, obviously, are made up by the addition of adequate amounts of carbonate or of caustic soda though such is not represented in the drawing.

Minor modifications of the general scheme may be made without detracting from the economic value of my process. It would thus be possible to eliminate entirely the second digestion passing directly to the high temperature phase. Or the acidification might be eliminated. Or the high temperature phase might be dispensed with, by re-cycling, in toto, the product after passing the acidifier. None of these would work as well as the one plan I have here called "preferred," but they would prove profitable nevertheless. All such modifications I consider as within the scope of my disclosure.

Having thus fully described my process, I claim:

1. The method of completely resolving a cellulose-lignin complex which comprises: digesting said complex with a solution of caustic soda and sodium sulphite, in conventional amounts and ratios, until the contained fiber shall have been liberated; separating said fiber from the spent liquor and re-cycling approximately one-half thereof to make fresh cooking liquor; adding caustic soda to the remainder until the caustic content shall be approximately three times as great by weight as the organic content; digesting said mixture at a temperature of between 100° and 150°C . until approximately one-third of the total resident methoxyl shall appear, in conventional analytic procedure, to be combined in aromatic form; re-cycling sufficient of digested material to supply the caustic requirements of the initial digestion; carbonating the remainder and separating the bicarbonate of soda formed; evaporating and crystallizing the resultant solution to obtain acetate, formate, sulphite and carbonate of soda; separating said crystals; commingling and separating the mother liquor from said crystallization with a solvent suitable for the extraction of the resident aromatics; commingling a part of said extracted liquor with previously obtained bicarbonate and lime to pro-

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duce caustic soda and re-cycling said caustic soda to wherever caustic soda is called for and in such amounts as called for in previously specified steps; commingling the remainder of the extracted liquor with caustic soda in such amount that it shall approximate three times the weight of the residual organics resident therein and digesting the mixture at approximately 200° C., until substantially all the acetyl groups resident therein shall be present as sodium acetate; commingling the resultant mass with sufficient water to dissolve the resident soda salts but leaving sodium oxalate in substantially undissolved form; separating said oxalate; crystallizing the resultant solution for the resident sodium acetate and formate; removing said crystals; carbonating the residual solution and separating the bicarbonate formed; extracting the resident aromatics in the residual solution with a suitable solvent for same, and re-cycling the extracted solution to undergo once more the caustic digestions prescribed herein.

2. The method of completely resolving a cellulose-lignin complex set forth in claim 1, with the additional

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proviso that the temperature in the initial digestion be also maintained at less than 150° C.

3. The method of completely resolving a cellulose-lignin complex set forth in claim 1, with the additional step that the solution undergoing the higher temperature caustic digestion be first purified from resident fats and resins by acidification and removal of the substances thus rendered insoluble prior to commingling with the amount of caustic soda required in said higher temperature digestion.

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