

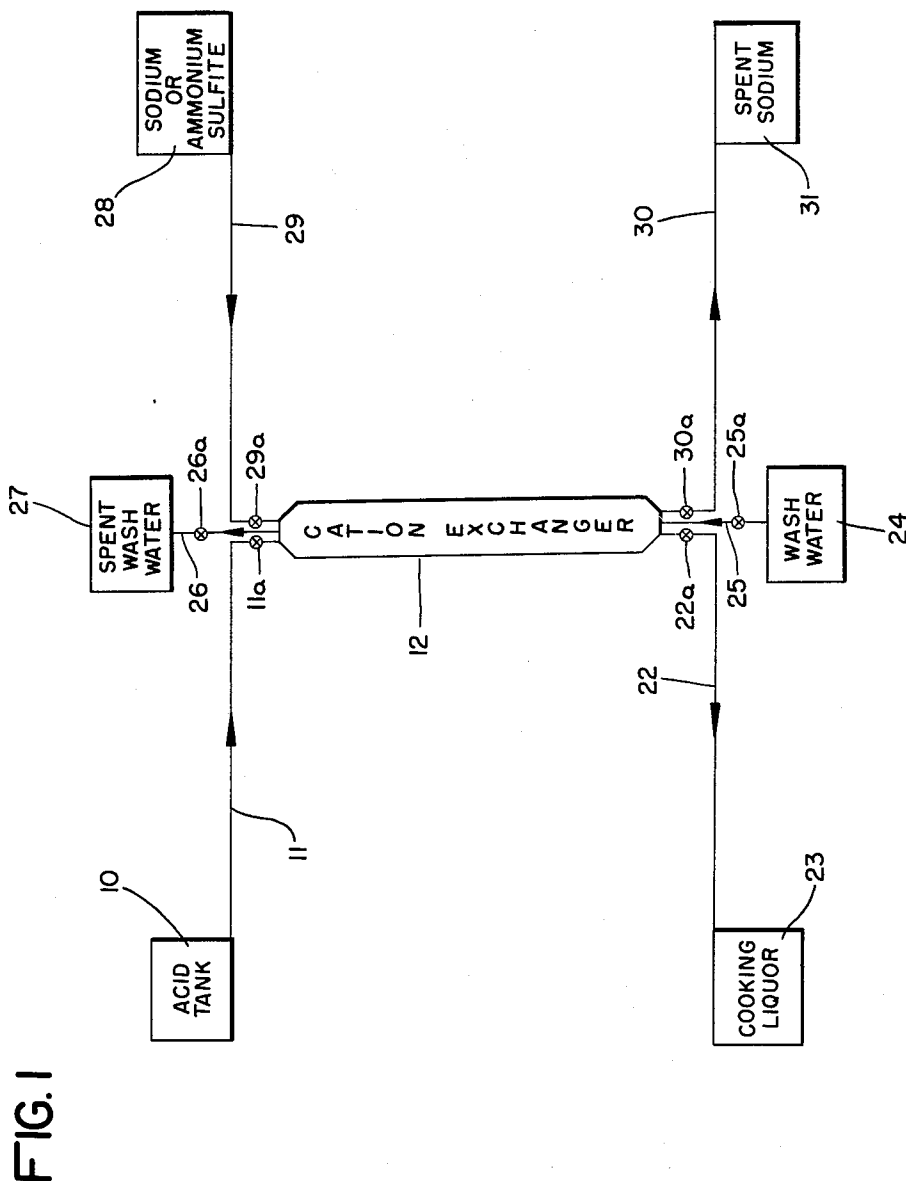
Feb. 28. 1956

G. HAYWOOD
METHOD OF PRODUCING SULFITE COOKING LIQUORS
AND RECOVERING VALUABLE
CONSTITUENTS THEREFROM

2,736,635

Filed July 7, 1951

3 Sheets-Sheet 1



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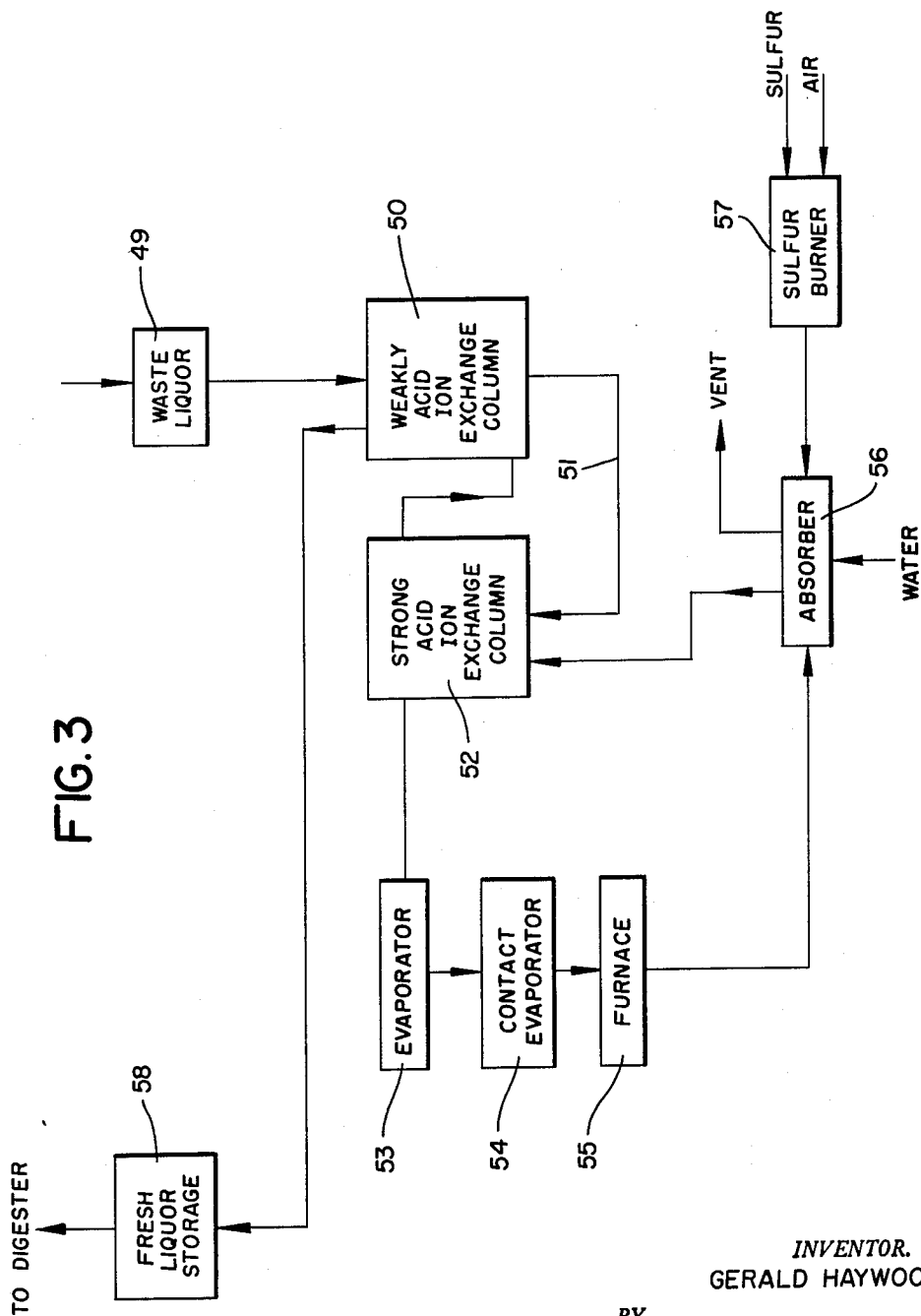
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METHOD OF PRODUCING SULFITE COOKING LIQUORS AND RECOVERING VALUABLE CONSTITUENTS THEREFROM

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5 Claims. (Cl. 23—129)

This invention relates to methods of producing cooking liquor for the production of paper pulp. It has reference to the production of sulfite cooking liquors of the type employed in making either semi-chemical sulfite pulp, full monosulfite pulp or acid sulfite pulp. The neutral sulfite cooking liquors, which are usually used in the pulping of hard woods by either a semi-chemical or a full monosulfite process, are produced from normal sulfites, while the acid sulfite cooking liquors, usually used in the cooking of softer woods, are largely solutions of acid sulfites with an excess of SO₂ present. The invention is particularly concerned with those cooking liquors of all three types, which have as their metallic or base component either sodium or ammonium, which are monovalent. Actually the so-called neutral sulfite liquors are not usually strictly neutral but are more nearly so than other types of cooking liquors which are distinctly acid or alkaline. Neutral sulfite cooking liquors frequently have a pH well above 7.0 and provide a waste liquor having a pH as high as 8.0.

The invention relates also to the cyclic production and use of such cooking liquors by a method in which the valuable ingredients are continuously recovered and re-used in the pulping of successive quantities or charges of wood or other cellulosic raw material.

It has long been appreciated that neutral sulfite cooking liquors, such as those consisting primarily of solutions of ammonium or sodium sulfite with a certain amount of the corresponding carbonate, are desirable from the standpoint of relatively high yields from the wood or other cellulosic source material and the production of a good grade of pulp. They are particularly useful in the pulping of hard woods. However, neutral sulfite cooking processes as heretofore practiced, particularly in mills not equipped to carry on kraft or sulfate pulp producing operations in conjunction with the sulfite pulping operations, have involved such heavy losses of the valuable constituents, such as the sodium, as to be substantially prohibitive from the standpoint of cost. The use of sodium or ammonium based acid sulfite cooking liquors has been restricted for similar reasons.

A primary object of the present invention has been to provide a method of producing and recovering cooking liquor in connection with semi-chemical, full monosulfite, or acid sulfite pulp producing processes, of the types indicated above, which will enable such processes to be operated with sufficient economy of the valuable components of the cooking liquor as to be commercially competitive with, and even less expensive than, other methods of producing sulfite pulp. It will be understood that the term "semi-chemical sulfite pulp" refers to that type of pulp which is produced by removing most of the lignins of the raw material, without removal of the pentosans and similar constituents, by cooking with a sulfite liquor and then forming the partially cooked material into a usable pulp by physical means, such as mechanical disintegrators and the like. The terms "acid sulfite pulp" and "full monosulfite pulp" are used to designate pulps

which are produced from wood or the like in a form usable for the production of paper or paper products through the use of a sulfite cooking liquor without the necessity of subsequent mechanical disintegration. The character of the cooking liquor, the quantity employed in the pulping of a given amount of the raw material and the length of time required for the cooking step differ in the three types of process.

In accordance with the present invention the sulfite cooking liquor is formed, at least in large part, by combining sodium or other desired base component with the desired acid or active component by a suitable ion exchange procedure. This involves contacting an appropriate cation exchange resin in the sodium or ammonium form with a sulfitic, acidic agent, such as sulfurous acid or a solution of sulfur dioxide in water, or the like, to bring about an exchange of hydrogen from the acid for at least a part of the sodium or ammonium component of the resin to produce sodium or ammonium sulfite or bisulfite. The resulting solution is in a form suitable for use, with or without subsequent concentration, dilution, additions or other treatment, as a neutral or acid sulfite cooking liquor, depending upon the conditions under which the exchange is carried out. In the preferred practice of the invention the sulfitic agent used in the foregoing procedure is in part derived from the waste liquor of a prior semi-chemical, acid sulfite, or full monosulfite cooking operation. A certain amount of sulfur dioxide is recovered or produced from such waste liquor and is dissolved in water to form at least a part of the acid required. So also, in the preferred practice the cation exchange resin, which has been converted from the sodium or ammonium form to the hydrogen form, by the foregoing procedure, is recharged with the sodium or ammonium ion by contacting it with the waste liquor, or components thereof, derived from a prior neutral or acid sulfite cooking operation. In this way a cyclic process is provided in which a continuous supply of cooking liquor is available for the pulping of successive batches of wood or other cellulosic material with the addition of only sufficient fresh liquor, or constituents thereof, as may be required to make up for losses in the cyclic operations. The reference to components of the waste liquor is intended to encompass the use of derivatives of waste liquor, such as green liquor produced by the concentration and smelting of the waste liquor and the dissolution of the smelt.

As will appear from the detailed description hereinafter, the present invention not only contemplates the removal of most of the sodium or other base constituent from the waste liquors but also certain other constituents, which are advantageously burned with the production of heat required in the operations. A certain amount of sulfur may be recovered in the course of such burning and in other ways.

The ion exchange may be carried out on strictly a batch basis, if desired, by the use of a large vessel or tank containing a suitable amount of exchange resin and into and from which the waste liquor and the acidic sulfitic agent are alternately introduced and removed. Preferably, however, a semi-continuous method is used, in which the waste liquor or the like and the acidic sulfitic agent are alternately passed through an elongated column containing the exchange resin.

It has been found advantageous, particularly in connection with pulping processes in which the waste liquor has a pH somewhat above 7.0, to employ two cation exchange columns in series for the recovery of the positive ions from such waste liquor and in the production of fresh cooking liquor for a succeeding cook.

Certain ion exchange resins have been found to be more efficient than others in the absorption of sodium or am-

monium from the waste liquor but, at the same time, the resins which are more efficient in this step have been found less efficient in the reverse operation, i. e., in the exchange of the sodium or ammonium ion for hydrogen in the course of producing the desired fresh cooking liquor. Strongly acid resins, such as those of the sulfonic type, have been found to be of this character. Other resins, of the weakly acid type, such as the carboxylic resins, have been found to present the reverse situation. Thus, they have been found to be readily convertible, with good efficiency, from the sodium or ammonium form to the hydrogen form upon contact with an acid, such as sulfurous acid, but they are less efficient in the reverse exchange. Accordingly, when a waste liquor is passed through a column containing such a resin there is danger of substantial leakage of the sodium or ammonium ion which will remain in the effluent from the column. Efficient recovery of the sodium or ammonium ions from neutral sulfite waste liquors and economical production of fresh neutral sulfite cooking liquor can be provided by the employment of two columns in series. The waste liquor may first be passed through a column containing the weakly acid exchanger which will remove a substantial portion of the sodium or ammonium ions. The effluent from the first column may then be passed through a second column containing an exchanger of the strongly acid type which will effectively remove substantially all of the remaining sodium or ammonium ions. In the subsequent recovery step the acidic agent, such as sulfurous acid or a solution of sulfur dioxide in water, may first be passed through the column containing the strong acid exchanger to remove a substantial part of the sodium or ammonium ions picked up by the latter in the preceding stage and the effluent may then be passed through the column containing the weakly acid resin where it will efficiently remove a high percentage of the sodium and ammonium ions absorbed in that column. It will be understood, of course, that the recovery of the sodium or ammonium ions will not be complete, but by the two-stage process described a quite high percentage of recovery will be effected. Furthermore, the effluent acidic agent from the second column may readily be made of a suitable character for use as a fresh neutral or acid sulfite cooking liquor for a succeeding cooking operation. By the use of sulfurous acid or other acidic sulfite agent of appropriate strength in the restoration of the beds of the two columns to the hydrogen form, the effluent from the final column may be satisfactory as a cooking liquor without material modification. However, if desired, the process may be so carried out that the effluent will require some modification either by way of concentration, dilution, or addition of other active ingredients prior to the use thereof as a cooking liquor.

With the foregoing purposes, features, and advantages in view, the invention will now be described in greater detail in conjunction with the accompanying drawings, in which:

Fig. 1 is a diagrammatic view illustrating a simple process for producing neutral or acid sulfite cooking liquor in accordance with the invention;

Fig. 2 is a diagrammatic view, in the nature of a flow sheet, illustrating a process by which fresh cooking liquor may be produced and utilized in the pulping of cellulosic material and by which a substantial portion of the valuable constituents may be recovered from the waste liquor and utilized in the production of new cooking liquor; and

Fig. 3 is a diagrammatic view, similar to Fig. 2, illustrating a modification of the process in which two ion exchange columns are employed.

Referring now to Fig. 1 of the drawings, there is illustrated schematically a simple arrangement of apparatus for carrying out the improved method of producing fresh sulfite cooking liquor. A tank 10 is provided for the storage of a suitable acid for use in the process. This may be sulfurous acid, or a solution of sulfur dioxide in water or a solu-

tion of an acid sulfite, i. e., a bisulfite, capable of exchanging its hydrogen for the sodium (or ammonium) ion originally present in the exchanger as will be explained. From the tank 10, the acidic material is led through a pipe 11, under control of valve 11a to the upper end of an ion exchange column 12. The latter is filled to an appropriate height with a cation exchange resin of any suitable type which is not soluble in or otherwise destructively affected by the acids and salt solutions to be passed through it. Numerous synthetic organic exchangers are available which are rendered insoluble, in the solutions or agents passed through them in accordance with the present invention, by cross-linking the resin skeleton into a vast molecular network similar to that encountered in thermosetting plastics. Suitable ionic groups are affixed to such resins. The resulting ion exchange resin may be either of the strongly acid type, such as a sulfonic resin (of the character sold by Dow Chemical Company, under the trade designation "Dowex-50") or of the weakly acid type, such as a carboxylic resin (of the character sold by Rohm and Haas Company, under the trade designation "Amberlite IRC-50"). Any of the resins hereinafter mentioned may be employed. Prior to the introduction of the acid, the resin should be placed primarily in the sodium (or ammonium) form as distinguished from the hydrogen form. If it is originally in the acid form, it may be converted to the sodium form by passing through it a solution of sodium chloride (in the case of a strongly acid exchanger), or a solution of sodium carbonate or sodium hydroxide (in the case of a weakly acid exchanger).

The acid solution from the tank 10 is preferably passed downwardly through the resin bed and is discharged through a control valve 22a and a line 22 to a cooking liquor storage tank 23. As explained below, the rate of flow of the acid solution through the resin bed should be such as to allow sufficient contact time to effect the desired exchange of the hydrogen of the acid solution for the sodium (or ammonium) of the resin. As a result of the ion exchange process within the column 12, a solution containing sodium (or ammonia) and free and combined sulfur dioxide will thus be delivered to the tank 23, and if the character of the acid solution and the quantity of the ion exchange resin in the column 12 are appropriately selected, the liquor delivered to the tank 23 will be suitable for use in a sulfite cooking operation. It should be understood that it is not necessary that the exchange of sodium (or ammonium) originally held by the resin for the hydrogen of the acidic material be complete. The extent to which the exchange may be satisfactorily carried will depend upon the character of the resin employed and the conditions under which the exchange is carried out. A resin of the weakly acid type such as the "Amberlite IRC-50" referred to above will be found capable of absorbing a relatively high percentage of the hydrogen ion of the acid, i. e., up to 90-100% in exchange for its sodium (or ammonium) ion. However, the more strongly acidic resins, such as "Dowex-50," will, as a practical matter be found capable of absorbing a lesser percentage of hydrogen ions of the acid in exchange for the sodium (or ammonium) ions of the resin. This percentage is usually not greater than 40%. It should also be understood that in the repeated use of the column in which it is alternately made to exchange basic ions for hydrogen and then made to exchange hydrogen for basic ions, it is only necessary that a part of the resin in the bed be so converted in each phase of the operation.

When the exchange of the basic ions of the resin for the hydrogen ions of the acid drops below a point which is commercially practicable and beyond which the effluent no longer forms a satisfactory cooking liquor, with or without economically feasible modifications, the flow of acid solution through the column is discontinued. Suitable modifications of the effluent from the column may include the addition of an appropriate amount of sodium

(or ammonium), carbonate or other alkaline solution based on sodium or ammonium. This will react with the excess acid to produce more sodium (or ammonium) sulfite and is preferably added in sufficient amount to give the liquor the desired pH.

To restore the resin in the column 12 to a condition in which a relatively high percentage of the resin is in the basic form, a solution containing sodium (or ammonium) ions may be passed through the resin. This solution may, for example, be salt brine, sea water, or other solution of sodium chloride, or may be a solution which contains sodium (or ammonium) sulfite, ammonium chloride, sodium carbonate, ammonium carbonate, or sodium or ammonium hydroxide or the like. As a source of the base ions, waste liquor from a sulfite cooking operation, or a derivative from such liquor, may be used. The solution having a suitable base ion content may be taken from a tank 28 and led through a line 29 controlled by a valve 29a to the cation exchange column 12. The operation may then be carried out in substantially the same manner as described above, but in the course of this stage, a portion of the base cations of the solution passing through the column 12 will be exchanged for the hydrogen absorbed by the resin during the preceding stage. The effluent during this stage of the process may be passed through the line 30, under control of the valve 30a, to a storage tank 31. Ultimate disposition of the liquid collected in the tank 31 will depend upon the character of the solution taken from the tank 28. If the latter is the waste liquor from a prior sulfite cooking operation, it may contain lignins and other wood components. In this case, the liquor in tank 31 may advantageously be evaporated and burned for the recovery of its sulfur content and the development of useful heat.

In a specific example of an operation in accordance with the foregoing, on a laboratory scale, a cation column formed of Pyrex glass 29 inches high and 4 inches in outside diameter was used. It was filled to an appropriate height with a resin of the strong acid type formerly sold by the American Cyanamid Company under the designation Ionac C-200 and now being sold by American Zeolite Corp. under the trade designation "Ionac C-200." It is a phenol formaldehyde sulfonate resin of a type which may be prepared in accordance with the teachings of the patent to Wassengegger No. 2,228,159, granted January 7, 1941. Approximately 1500 grams of the resin were employed. The column was first backwashed by passing water upwardly through it from a tank 24 (Fig. 1) this being introduced through a line 25 controlled by a valve 25a and the effluent being passed through a line 26, controlled by a valve 26a, and passed to a tank 27 or discarded. A solution of hydrochloric acid was then passed through the column in the same manner as the backwash water to convert the resin to the hydrogen form. The effluent from this operation was also discarded. After rinsing the exchange resin, and discharging the wash water, a solution of sodium sulfite was passed through the column. This solution was formed by adding 110 grams of anhydrous sodium sulfite to eleven liters of distilled water. The solution was passed through the column at the rate of five gallons per hour. The effluent had a pH of 1.8 and smelled strongly of SO₂. It was primarily a solution of SO₂ or sulfurous acid. Another batch of eleven liters of sodium sulfite was then passed through the column at the same rate. The final effluent, i. e. the last 100 milliliters had a pH of 7.9 and had little odor of SO₂, thus indicating that the column was near exhaustion. A substantial part of the sodium from the sodium sulfite had been exchanged for the hydrogen ion of the resin. The resin was then restored largely to its hydrogen form by passing through it a solution containing 155 grams of SO₂ in eleven liters of distilled water. 6740 milliliters of this solution was passed through the column to regenerate the cation bed. At the end of this operation the solution coming off had a pH of 1.9, indicating that little further

exchange was taking place in the resin bed and most of the SO₂ in solution was passing through without exchange of its hydrogen ion for sodium. The pH of the entire effluent from this operation was 2.9 and the effluent contained a large part of the sodium absorbed by the bed in the preceding step of the process. This effluent was readily usable as a cooking liquor for wood chips or the like and by the addition of a suitable amount of sodium carbonate was readily capable of being made to conform with the cooking liquors commonly employed in neutral sulfite pulping operations of either the semi-chemical or the full monosulfite types. The bed was then rinsed with distilled water and another ten liters of a sodium sulfite solution of the same concentration as that previously used was again passed through the resin bed. At the end of this run, the effluent had a pH of 6.2 and did not smell of SO₂, indicating that the bed had been exhausted of its readily exchangeable hydrogen ion.

From the foregoing procedure it was determined that the capacity of the bed for exchange of its hydrogen ion for the sodium ion was greater in the first run than in the second, thus indicating that the intervening charge of the bed was not complete. This indicated that complete conversion of the resin to the hydrogen form with the solution of SO₂ should not be attempted. In other words, the bed should at all times be partly in the sodium form and the successive stages of a cyclic process should simply alternate the ratio of the two forms. This is the case for a strongly acid cation exchanger and an essentially neutral sodium solution. However, other operating conditions should be maintained for other exchange resins or other end results in the use of solutions of SO₂ in the production of the desired sulfite.

The following principles may be stated with respect to a continuous cyclical process:

For a strongly acid exchanger subjected in one stage to a neutral sodium solution, the bed should at all times be partly in the sodium form and partly in the hydrogen form.

For a strongly acid exchanger subjected in one stage to an alkaline sodium solution, the bed should at all times be at least partly in the sodium form.

For a strongly acid exchanger subjected in one stage to an acid sodium solution, the bed should at all times be at least partly in the hydrogen form.

For a weakly acid exchanger subjected at one stage to a neutral sodium solution, the bed should at all times be at least partly in the hydrogen form.

For a weakly acid exchanger subjected at one stage to an alkaline solution, the bed should at all times be partly in the sodium form and partly in the hydrogen form.

These conditions may be altered somewhat by extreme acidity or alkalinity of the sodium solution, by extreme concentration or dilution or excesses of the SO₂ solution, by extreme concentration or dilution or excesses of the sodium solution, or by changes in the acidity of the cation exchanger. However, it has been determined by a number of experiments that the sodium (or ammonium) solution used to charge the resin should not be less concentrated than 0.2 N nor more concentrated than 3 N in sodium (or ammonium or their sum if both are used) and the solution of SO₂ should not be less concentrated than 0.2 N nor more concentrated than 2 M in SO₂ in order that the exchanger be effectively charged with and discharged of its base content without using excessively large quantities of solutions and chemicals, without interfering with the efficiency of the exchange, and in order that a cooking liquor suitable for the digestion of wood chips be produced.

Similarly it has been found that it is best to have each volume of solution in contact with the cation exchanger for at least three minutes in order that the exchange of ions take place satisfactorily. More than thirty minutes of contact is usually not beneficial.

We turn now to the application of the invention to a cyclic pulping operation in which a desired part of the resin is restored to its sodium or ammonium form by the use of waste neutral or acid sulfite liquor, or a derivative therefrom, and fresh cooking liquor is formed by the use, at least in part, of constituents recovered from a prior cooking operation. It is common in the neutral sulfite pulp industry to use a cooking liquor based on sodium and containing carbonate and sulfite in such proportions as to have a pH of 10.5 to 11.5. Neutral sulfite liquors are commonly used in two types of pulping processes, the one (so called semi-chemical) relying on both chemical and mechanical reduction of the wood and the other (so called full monosulfite) using only chemical reduction. A typical liquor for semi-chemical pulping, which accomplishes part of the reduction of the pulp by mechanical means, comprises about 16% sodium sulfite and about 3 to 4% of sodium carbonate on the basis of the weight of the wood. The sodium sulfite concentration may be 4 to 5% of the weight of the water. About 600 to 700 pounds of chemicals per ton of pulp are required. If the digestion with this liquor is conducted under proper conditions and the pulp finally defibered by mechanical disintegration, only about 30% to 35% of the wood is dissolved and the resulting pulp has desirable properties. About 200 to 300 pounds more pulp are obtained per cord of wood than when full chemical digestion is employed. Even with these apparent advantages, the cost of semi-chemical pulp produced with neutral sulfite liquors would be excessively high in the absence of a suitable recovery method for the chemicals used. The waste liquor from this process is slightly alkaline and has a pH of between about 7.5 and 8.5.

A typical liquor for full monosulfite pulping comprises about 40 to 45% sodium sulfite and about 1 to 2% (preferably about 1.3%) sodium carbonate on the basis of the weight of the wood. The sodium sulfite concentration may be 10-12% of the weight of the water. About 1530 pounds of Na_2CO_3 and 455 lbs. of sulfur, per ton of pulp are required.

After the reduction of the wood, the defibered cellulose is separated from the cooking liquor and washed to remove most of the soluble and colloidal content. The spent cooking liquor and concentrated wash water are combined and ordinarily contain most of the cooking chemicals (the remainder having been lost in washing), solubilized lignin and other wood components. This solution with its suspended materials is known in the trade as neutral sulfite waste liquor and because of its organic content and lack of active sulfite ions is for the most part not reusable.

In the acid sulfite process the active agent is free sulfurous acid. There is very little base in the cooking liquor. A usual composition is 50 grams per liter of free SO_2 (as sulfurous acid) and 10 grams per liter of combined SO_2 (as sodium sulfite). Pulp can be obtained with a liquor that contains no base by cooking for a relatively long time at 110° C. Presence of the base, however, permits cooking at higher temperatures without "burning" the wood chips. Roughly one-half of the free SO_2 in the cooking liquor cycles between the digester and the acid making system and thus never gets into the waste liquor. The waste liquor is always acid, with a pH between 2 and 3. A pulp yield of about 45 to 50% of the wood is obtained.

In accordance with the present invention at least a part of the cooking chemicals in the waste liquor is recovered in a condition suitable for reuse in cooking by replacing part of the cation base of the waste liquor with hydrogen ions by means of either a strongly acid or a weakly acid exchanger, until the capacity of the exchanger for further replacement has been carried to the economically practical extent, part of the cation base, being absorbed, on the exchanger. Subsequently the exchanger is reconverted to its original condition, thereby eluting the cation base, with a solution which will contain, after

the reversion, a quantity of free and combined SO_2 equal to that originally present in the cooking liquor from which the waste liquor is derived.

Hydrogen exchanger as used herein refers to a solid material which is capable of absorbing metallic ions from solutions thereof and replacing them with hydrogen ions and is also capable of being reconverted, at least partially, with acid solutions. Suitable hydrogen exchangers for this invention are synthetic cation exchange resins such as those described in U. S. patent to D'Alelio No. 2,366,007, granted April 12, 1949, substantially in the hydrogen form. These resins are of the strongly acid, sulfonic type. The resins may, for example, be sulfonated copolymers of polystyrene and di-vinyl benzene. Various resins of this character are sold under the trade designation "Dowex-50" (Dow Chemical Co.), "Permutit Q" (Permutit Co.), "Amberlite IR-120" (Rohm & Haas Co.), "Nalcite HCR" (National Aluminate Co.), "Duolite CS-20" (Chemical Process Co.) and "Ionac C-240" (American Zeolite Co.). In lieu of the foregoing strongly acid resins there may be employed the weakly acid, carboxylic type resins which are usually polyacrylates. Suitable resins of this character may be made in accordance with the teachings of D'Alelio Patent No. 2,340,111, granted January 25, 1944. A typical resin of this character is that sold under the trade designation "Amberlite IRC-50." Such weakly acid resins may be used effectively, however, only when the waste liquor or a derivative from such liquor is at a pH of 8.0 or above during the major portion of the exchange for the regeneration of the partially exhausted resin to the base form. Suitable acidic sulfite bearing agents which are capable of discharging the cation base from the resin in the production of cooking liquor, are solutions of sulfurous acid in water or solutions of SO_2 in water, either alone or in conjunction with gaseous SO_2 . For the reversion of the weakly acid resins to the hydrogen form there may be used, in addition to or in lieu of the solutions of sulfurous acid in water or solutions of SO_2 in water, solutions of bisulfites which are capable of releasing hydrogen in exchange for the cation base of the exchanger acquired from the waste liquor. All of the foregoing reconverters are referred to hereafter as available sulfurous acid or solutions having available sulfurous acid.

As shown above, fresh cooking liquor contains a definite requisite quantity of the cation base (which may be ammonium in place of or in addition to sodium) and has in addition a required sulfite content. Therefore, in the reversion there is used a quantity of available sulfurous acid which will contain in the effluent a quantity of free and combined SO_2 equivalent to this sulfite. (By free SO_2 we mean that which may be volatilized from a boiling solution.) In the normal use of the method of this invention, the removal and replacement of the hydrogen ions are repeated, and in a continuous operation, the quantity of cation base eluted in the reversion or replacement is substantially equal to that absorbed in the exchange for and removal of hydrogen.

In the usual manner of operation, the hydrogen of the exchanger is not completely exhausted or restored; not all of the cation base is absorbed and not all of the acidity of the reconverter is utilized. The separated spent reconverter is therefore neutralized by the addition of the hydroxide or carbonate of the cation to bring the cation content to the desired point for cooking liquor purposes.

It is known in the art of ion exchange that exchange reactions are less efficient in concentrated solutions. This inefficiency is due largely to an effect known as Donnan absorption, the absorption of quantities of salt, at high concentrations of solutions, above the ions absorbed by the exchange reaction proper. This effect is manifested, for example, when a cation exchanger substantially in the sodium form is immersed in a con-

centrated solution of a sodium salt. Sodium salt from the solution is found to diffuse into the exchanger until an equilibrium is attained in which the concentration of the external solution has been reduced and the exchanger contains substantial quantities of salt. Consequently in ion exchange reactions in concentrated solutions, the average effluent solution is less concentrated than the influent, and the exchanger—especially in the case where a reaction is possible between the hydrogen removing solution and the hydrogen replacing solution—may have to be washed free of diffused salt between the two stages to prevent unwanted side reactions. Because of this effect, in the method of this invention an inefficiency occurs in the absorption of the sodium or ammonium base from the waste liquor and in its recovery with available sulfurous acid. It is therefore necessary to increase the amount of the agent used in the recovery step to correct for this inefficiency, in order to obtain a fresh cooking liquor containing the requisite amount of sulfite ion. The extent of this correction will be illustrated in the examples.

However, in some cases one need not wash the exchanger between the removal and replacement of the hydrogen since the Donnan salt absorbed from the waste liquor constitutes only a small recycle of waste liquor to the fresh cooking liquor. Similarly it is not necessary to wash the column between the hydrogen replacement step and the hydrogen removal step unless it is desired to remove the sulfurous acid. It is best to use dilute available sulfurous acid in the hydrogen replacement step in order to increase the efficiency of elution, although it is desirable to use a sufficient concentration that the neutralized spent recovery agent will have a concentration of sulfite equal to or greater than that required in the fresh cooking liquor. In order to increase the concentration of sulfite in the neutralized spent recovery agent, it is usually more advantageous to concentrate the available sulfurous acid than to concentrate the spent recovery agent forming the effluent.

According to a preferred method of this invention, the waste liquor is passed through a column or bed of cation exchange resin which is partially in the hydrogen form and subsequently the resin is restored to its original form and the absorbed sodium or ammonium is recovered from it while the resin is in the column. It has been found that particularly efficient operation is obtained when the waste liquor is passed through the column in one direction and the recovery agent is subsequently passed in the opposite direction. Under some circumstances however the waste liquor and the recovery agent may advantageously be passed in the same direction.

In Fig. 2 there is schematically shown, in the form of a flow sheet, a procedure and suitable apparatus for the recovery of sodium or ammonium and of sulfur from the waste liquor of any of the pulping processes indicated above and the use of the recovered constituents in the production of fresh cooking liquor.

Referring to Fig. 2, the digester is indicated schematically at 30. Wood chips or other source of cellulosic material is charged into the digester and fresh liquor is introduced from a storage tank 31. Digestion is carried out under such conditions of temperature and pressure as are normally employed in semi-chemical, full monosulfite or acid sulfite pulping operations. The character of the liquor employed will depend upon whether the process is of the semi-chemical type, the full monosulfite type, or the acid sulfite type. After the digestion has been completed the contents of the digester are blown into a blow tank 32 from which it is led, in the case of semi-chemical pulp, to a disintegrator 33 and then to a knotter 34. In the case of full monosulfite and acid sulfite pulp the disintegrator is eliminated since the reduction of the wood to the pulp form is completed in the digester. From the knotter any incompletely digested portions of

the raw material are separated from the plup. The pulp is passed to a washer 35 which is preferably of the sectional type in the first section of which the pulp is washed with strong filtrate taken from a tank 36. This filtrate in passing through the pulp washes out the spent cooking liquor and various salts and colloids mentioned above. This constitutes the waste liquor of the process and is passed to a waste liquor tank 37. In the second section of the washer the pulp is washed with a weaker filtrate taken from a tank 38. This in passing through the washer forms the strong filtrate which is delivered to the tank 36. The partially washed pulp passing from the washer 35 is then passed to a second washer 39 in the first section of which it is washed with a still weaker filtrate taken from a tank 40 and which, after passing through the washer 39, is discharged to the tank 38. In the second section of washer 39 the pulp is washed with plain water and the filtrate from this operation is discharged to the weak filtrate tank 40. The clean pulp emerging from the second washer is delivered to a raw pulp storage tank 41.

A portion of the waste liquor may be delivered from the tank 37 directly to the fresh liquor storage tank 31 for reuse along with the fresh liquor in a subsequent digestion operation. This is for the purpose of reducing the load on the ion exchange column to be described. However, the major portion of the waste liquor is delivered from the tank 37 to an ion exchange column 43 containing one of the resins hereinabove mentioned, primarily in the hydrogen form. The effluent from the column, in this stage of the process, is sent to an evaporator 44 and then to a contact evaporator 45; the residue from the latter is passed to a furnace 46 wherein it is burned to generate heat from the lignins and other burnable constituents. A certain amount of SO_2 is liberated in the furnace and this is passed to an absorber 47 in which it is absorbed by cold water that is also introduced into this member. Other gases of the combustion in the furnace 46, such as carbon dioxide and nitrogen, are discharged from the absorber through the vent line indicated. The absorber may suitably be a tower packed with Raschig rings or other acid resistant material, through which the gases are passed upwardly and cold water is passed downwardly.

Subsequently the resin in the ion exchange column, which has been partially exhausted of its hydrogen, is restored to its hydrogen form by passing the solution of sulfurous acid or of SO_2 from the absorber 47 into the column. Since a substantial portion of the sulfur initially present in the fresh cooking liquor is lost in the various stages of the process explained above, additional sulfur dioxide is introduced into the absorber from a sulfur burner 48. Here sulfur and air are introduced and the resulting gases have a sufficiently high concentration of sulfur dioxide to provide, at the liquid outlet of the absorber, available sulfurous acid suitable for the restoration of the resin in the column, to the desired extent, to the hydrogen form. However, since it may be difficult to provide, by the method explained, available sulfurous acid of sufficient strength to produce an effluent from the exchange column having the concentration of sulfites normally desired for cooking purposes the solution derived from the absorber may be concentrated before it is sent to the column. As explained, the restoration of the resin is only partially completed so that it remains partly in the sodium or ammonium form but it is restored sufficiently to the hydrogen form to serve effectively in a repetition of the first exchange operation. It will be understood that in the continuous operation of the system the resin will be alternately converted from and to its primarily hydrogen form to and from its primarily cation base form. The effluent from the hydrogen restoring step is passed to the fresh liquor storage tank 31.

By appropriate conduct of the operations, i. e., control of the extent of removal of the hydrogen of the resin during contact with the waste liquor and the extent of

replacement of the hydrogen during contact of the resin with the available sulfurous acid and the employment of available sulfurous acid of appropriate concentration in the hydrogen restoration step, the effluent from this step will provide a fresh liquor of suitable character for use in a subsequent digestion operation. It will be understood, however, that if this effluent is not of the character desired for digestion purposes it may suitably be modified by concentration or dilution with or without the addition of other chemicals such as sodium carbonate and the like. Usually it will be found necessary or desirable to add sodium carbonate or sodium hydroxide or other alkaline solution of a sodium compound to the effluent for the purpose of neutralizing the residual acids of the available sulfurous acid employed in the hydrogen restoring step. In the use of a strongly acid exchange resin it will be found that bisulfites are created in the hydrogen restoring step which should also be neutralized. Furthermore, as has been indicated, a neutral sulfite cooking liquor should normally contain a certain amount of sodium carbonate or the like to raise the pH of the liquor to a point between 10.5 and 11.5. Therefore, sufficient sodium carbonate or the like to achieve this result should be added to the effluent from this step of the process before it is passed to the storage tank 31, when a neutral sulfite is desired. Moreover, the cation base content of the liquor passed to the storage tank should be sufficiently above that actually desired for cooking purposes to offset the diluting effect of the portion of the waste liquor passed directly from the tank 37 to the tank 31.

It will be understood that the apparatus employed in the process above described will include, in addition to the particular items described and schematically indicated in Fig. 2, such items as pumps, valves, vents, condensers, coolers, boilers, precipitators, agitators, motors, blowers, storage vessels, and similar auxiliary equipment, to enable the various procedures explained to be properly carried out. The direction of flow of the various gases and liquids should be such as to facilitate the particular operations involved. Thus, in the operation of the ion exchange column it has been found desirable to pass the liquids upwardly through the column when gases are evolved as a result of the ion exchange. Even in the absence of such gas evolution it is often desirable to provide upward flow of the liquids to offset the tendency of the resin to become compacted due to swelling in the course of the reaction.

By way of illustration of suitable conditions for various operations or steps in the process described above in connection with Fig. 2, the following examples are given:

Example 1.—In carrying out a portion of the complete process on a laboratory scale, a small ion exchange column having a diameter of 1.9 centimeters and a cross sectional area of 2.9 square centimeters was charged with 50 grams of "Amberlite IR-120." The height of the resin in the column was 30 centimeters. A waste liquor was passed through the column, this liquor containing lignosulfonates, sodium sulfite, and sodium bicarbonate. The sodium concentration of the liquor was .38 N. The pH was 7.2. The liquor was passed through the column at the rate of 24 ccs. per minute. Complete absorption of the sodium from the liquor took place until a break through of sodium occurred when approximately 85% of the maximum sodium capacity of the resin had been reached. Approximately 350 milliliters of the waste liquor had been passed through the column up to this point. When additional waste liquor was passed through the column the percentage of sodium absorbed dropped rapidly so that after 500 milliliters of the liquor had been passed the percentage of sodium absorbed was only about 18% of that present in the last 25 milliliters of the liquor. By the time 700 milliliters of the waste liquor had been passed through the column substantially no absorption of sodium was found to take place. This indicates the desirability of passing only about 350 milliliters

of the waste liquor through a body of 50 gms. of the indicated resin under the conditions set forth. The presence of the lignosulfonates in the waste liquor did not appear to interfere with the exchange.

Example 2.—In another operation in accordance with the above described process, on a laboratory scale, an ion exchange column having a diameter of 1.3 centimeters and a cross-sectional area of 1.3 square centimeters was filled to a height of 25 centimeters with 21 grams of a weakly acid cation exchanger based on carboxylic active groups. The specific resin employed was that sold under the trade designation "Amberlite IRC-50" marketed by Rohm & Haas Company. It is described as polymethacrylic acid. This resin was in the hydrogen form. A waste liquor similar to that used in the foregoing example was used, but one having a sodium concentration of 0.44 N. The pH was 7.7. This liquor was passed through the column at 2 to 6 ccs. per minute. It was found that initially about 25% of the sodium was absorbed on the resin. After 100 milliliters of the liquor had been passed through the column the percentage of absorption decreased gradually until only about 20% was being absorbed after 500 milliliters had been passed through the column. This indicates that the weakly acid resins when used alone can be expected to recover only about 25% of the cation base values of the waste liquor under the conditions mentioned. Even such recovery may, however, be economically advantageous under certain circumstances.

Example 3.—For the regeneration or reconversion of the strongly acid cation exchange resin used in Example 1, the resin in the column was converted to the complete sodium form with sodium chloride solution and then washed free of salt held by Donnan absorption. An aqueous solution of SO_2 having a concentration of 0.55 M was passed through the column at a rate of 12 cc. per minute (1 gallon per square foot per minute). It was found that after 50 cc. of the acid solution had passed, the effluent was 0.40 N in sodium; after 160 cc. the effluent was 0.30 N in sodium; and at 250 cc. the effluent was 0.26 N in sodium. From this point on, the sodium normality of the effluent decreased slowly, reaching 0.17 N after 550 cc. of effluent at which point 60% of the sodium content of the resin had been removed.

Example 4.—Regeneration or reconversion of the resin in the column of Example 2 was carried out in the same manner as described in Example 3, using 0.69 M H_2SO_3 ; the resin bed having been converted to the complete sodium form with 1 N sodium hydroxide and then washed free of absorbed hydroxide. It was found that at the commencement of this operation, the H_2SO_3 molarity and the total molarity of the effluent was very low compared to that of the influent; after 30 cc. of effluent, the concentration of H_2SO_3 was 0.05 M. The concentration of H_2SO_3 was 0.21 at 60 cc. effluent, and 0.62 M at 90 cc. effluent at which time 90% of the sodium in the resin had been removed.

From the foregoing it is clear that the strongly acid exchange resin of Example 1 is restored to its hydrogen form with much greater difficulty than the weakly acid resin of Example 2. It is commercially practicable to restore the strongly acid resin to the extent of only about 60%, while the weakly acid resin may be restored to the hydrogen form to the extent of between 90 and 100%. Since the strongly acid resin is highly efficient in exchanging its hydrogen ions for the sodium ions of waste liquor of the character indicated, but is inefficient in the reverse process of exchanging its sodium ions for the hydrogen ions of the regenerating sulfur dioxide solution, it is desirable to so operate a column containing this resin as to alternately convert the resin to the condition in which it is 25 to 60% in the hydrogen form and 40 to 75% in the sodium form and to the condition in which it is 0 to 20% in the hydrogen form and 80 to 100% in the sodium form. The weakly acid type resin, on the other hand,

because of its poor efficiency in absorbing sodium ions and high efficiency in absorbing hydrogen ions, under the conditions involved in this example, should be alternately converted from and to a condition in which it is 90 to 100% in the hydrogen form and 0 to 10% in the sodium form to and from one in which it is 40 to 80% in the hydrogen form and 20 to 60% in the sodium form.

It has been found possible to make more efficient use of the cation exchange resins by employing two ion exchange columns in series for the recovery of sodium or ammonium ions from the waste liquor of a neutral or acid sulfite pulping operation and to produce fresh liquor for further digestion purposes. In Fig. 3 there is illustrated schematically an arrangement of two ion exchange columns in series in relation to a pulping system similar to that shown in Fig. 2. It will be understood that the apparatus and operations illustrated in Fig. 3 serve simply to replace the corresponding portions of Fig. 2 and that the other apparatus and procedures indicated in Fig. 2, by which the pulp is produced and the waste liquor derived therefrom, are coupled in the same manner with the flow diagram of Fig. 3. As in the case of Fig. 2, various accessory pieces of equipment, such as pumps, valves, and the like have been omitted from the schematic showing of the process.

The waste liquor from a sulfite pulping operation of the character indicated in Fig. 2 is delivered to the waste liquor storage tank 49. From this tank the waste liquor is passed through an ion exchange column 50 containing a weakly acid exchange resin, preferably of the carboxylic type, such as "Amberlite IRC-50." The effluent from the column 50 is passed through a line 51 to a second ion exchange column 52 containing a strongly acid exchange resin, preferably of the sulfonic type, such as "Amberlite IR-120." The effluent from column 52 is passed to an evaporator 53 and then to a contact evaporator 54 and the residue is passed to a furnace 55. Any sulfur dioxide released from the effluent in the evaporators may be collected in a suitable absorption system for reuse. So also, any sulfur dioxide developed in the burning of the residue in the furnace 55 may be similarly recovered while the heat generated in the furnace may be used for the production of steam and the development of heat for other purposes required by the pulping operation. In the drawing the combustion gases developed in the furnace 55 are shown as being passed to an absorber 56 for the removal of the sulfur dioxide content, while the inert gases, such as carbon dioxide, nitrogen, and the like are vented from the absorber.

After the resins in the two columns 50 and 52 have been converted to a practicable extent from their original hydrogen form to the sodium or ammonium form, by the foregoing procedure, the resins are reconverted to the hydrogen form. For this purpose, sulfurous acid or a solution of sulfur dioxide in water may be produced in the absorber 56 with the desired strength of normality. This is accomplished by the absorption of the SO_2 from the furnace gases and the absorption of additional SO_2 developed in a sulfur burner 57. Cold water is supplied to the absorber in the manner described in connection with Fig. 2. The resulting solution of SO_2 may be further concentrated, if desired, and then passed through the resins in the columns 50 and 52. This may be done in parallel, if desired, but it is preferably done in series, as indicated in Fig. 3. The fresh SO_2 solution from the absorber is first passed through the column 52 and then through the column 50. If the parallel arrangement is employed, the effluent from both columns may be combined and passed to a fresh liquor storage tank 58. When the series arrangement is employed, the final effluent from column 50 is passed to the tank 58. In either case the effluent may be concentrated, if desired, before delivery to tank 58. It should be understood that the points of introduction and removal of the various influents and effluents are not intended to be indicated in

Fig. 3. The liquids may be passed either upwardly or downwardly within each of the ion exchange columns as may be best suited for the particular operations.

In the operation of the system of Fig. 3 the recovery of sodium or ammonium from the waste liquor will be only partially completed in column 50. Only about 20 to 30% recovery will be effected in this column. However, the base cation which passes through the column 50 will be caught in the column 52 to effect substantially complete removal of the sodium or ammonium from the waste liquor.

Since, as explained above, the weakly acid resin in column 50 may be readily restored almost completely to the hydrogen form and since the strongly acid resin in column 52 absorbs only a relatively small part of the hydrogen ions of the acid solution in the course of the reconversion step, it will be found that the effluent from column 52 will have adequate normality of sulfurous acid to effect good reconversion of the resin in column 50. It will be understood that in the use of the two columns, just as in the use of the single column, it is desirable to effect only partial conversion of the resins from the hydrogen form to the cation base form and vice versa. Moreover, the extent of recovery of the cation base ions from the waste liquor is higher.

A typical laboratory operation of a two column system in accordance with the form of the invention illustrated in Fig. 3 is as follows:

Two small ion exchange columns each having a diameter of 1.3 cm. and a cross-sectional area of 1.3 cm.² were filled with resin in the hydrogen form. The strongly acid column contained 30 g. of "Dowex-50" (having a moisture content of 40% of H_2O) and was filled to a height of 28 cm. The weakly acid column contained 21 grams of "Amberlite IRC-50" (having a moisture content of 50% H_2O) and was filled to a height of 24 cm. A 500 cc. sample of a waste liquor containing lignosulfonates, sodium sulfite, and sodium bicarbonate, having a pH of 7.2 and containing 8.7 milligrams of sodium per cc. was passed upwardly through the weakly acid column and thence downwardly through the strongly acid column. This quantity of waste liquor contains an amount of sodium ions equivalent to the capacity of the ion exchange beds. The effluent from the strongly acid exchanger bed had a pH of 1.0 showing substantial removal of sodium. The columns were then washed free of waste liquor with water and drained free of excess water. A 120 cc. portion of 0.55 M H_2SO_3 was passed downwardly through the strongly acid exchanger and then downwardly through the weakly acid exchanger. The exchanger was drained free of solution. This sulfite solution was 0.37 N in sodium showing that 1040 milligrams of sodium had been removed. The sodium recovery was 24% overall, that is, of the sodium in the waste liquor, 24% appeared in the sulfite solution. This sulfite solution was suitable for the digestion of wood chips. While this overall recovery appears to be rather low, it is, in fact, a definitely worthwhile recovery of sodium from the waste liquor. Some of the apparent loss of sodium is due to the fact that the resins were initially in the completely hydrogen form, whereas they retained a substantial percentage of sodium on reconversion to the hydrogen form. This apparent loss would not occur on repetitions of the same steps in a semi-continuous process. Overall recoveries as high as 40% may be obtained in such a process. Moreover, the recovery may readily be increased by varying certain of the operating conditions and procedures. For example, it has been found that the two column system may be operated with higher efficiency in the recovery of sodium from a liquor or solution which is more alkaline than that employed in the example. Recoveries as high as 60% may be obtained from alkaline solutions containing sodium. Furthermore, the percentage of recovery is affected by the ratio of the waste liquor passed through

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the columns to the quantities of the two resins employed in the columns. Thus, if only 370 milliliters of the waste liquor were passed through the columns on succeeding cycles, under the conditions of the example, utilizing the same quantity of sulfurous acid, the percentage of sodium recovered would be about 32%. So, also, substantially higher recoveries of sodium, up to 90%, could be effected if the cooking liquor to be produced were of the acid sulfite type. This would be of particular value in a mill which conducts both neutral and acid sulfite pulping operations.

As illustrative of the foregoing, the following further example is given:

In another laboratory scale operation in which two exchange columns, containing different types of resins, were utilized in series the first column had a diameter of 1.3 centimeters, with a cross-sectional area of 1.34 sq. cm., and a height of 22 centimeters. This was filled to a suitable height with a resin of the carboxylic type sold under the designation "Amberlite IRC-50." This column contained 21 grams of such resin having a 50% water content and a capacity of 4 meq./gm. The other column had a diameter of 1.9 cm., providing a cross-sectional area of 2.83 sq. cm., and a height of 25 cm. This was filled to a suitable height with a strongly acid type of resin, sold under the trade designation "Dowex-50," and contained 50 grams of the resin having a 40% water content and a capacity of 3 meq./gm. The resins in the two columns were placed initially in the complete sodium form. The "Dowex-50" was put in this form by contact in the column with an excess of 4 N sodium chloride solution. After such contact the resin was washed free of chloride with distilled water. The IRC-50 resin was put in the sodium form by contacting it in the column with an excess of 1 N sodium hydroxide solution and then washing with distilled water until the effluent had a pH of 9.

With the resins thus in the completed sodium form, 340 cc. of sulfurous acid, having a concentration of 0.55 M, were then passed downwardly through the two columns in series, it being passed firstly through the Dowex-50 resin and then through the IRC-50 resin. A flow rate of approximately 10 cc. per minute was maintained. The effluent from the Dowex-50 column was found to be 0.22 N with respect to sodium and 0.44 N with respect to hydrogen. This effluent had 75 meq. of sodium or 50% of the total exchangeable sodium carried by the resin. It had 150 meq. of hydrogen. After passage of this effluent through the IRC-50 column it was 0.45 N in sodium and 0.19 N in hydrogen. The meq. of sodium eluted in this column was 84, so that the reconversion of the bed to the hydrogen form was 100%. The total ionic strength of the final effluent was 0.64 N or 0.32 M. This indicates that there was a 45% loss in total ionic strength. The Donnan absorption of the sulfurous acid in the "Dowex-50" column was 40%, i. e. this percentage of the total input was not accounted for in the effluent. In the IRC-50 column the Donnan absorption was only 5%.

While various embodiments of the invention have been described in considerable detail, it will be understood that other embodiments or modifications than those specifically suggested are within the scope of the invention as defined by the appended claims. The apparatus and procedures specified for the various steps of the several processes disclosed are to be understood as being merely illustrative and not restrictive. A variety of different cation exchange resins of the character of those specifically mentioned herein may be employed in the various columns disclosed. Where specific resins have been mentioned, resins of the same strongly or weakly acid types may be substituted therefor. The two column process is particularly well suited for use in the production of either semi-chemical or full monosulfite pulp. For the acid sulfite process only the strongly acid or sulfonic

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resin should be used since the acid sulfite cooking liquor contains so much free SO_2 , which is in part derived from the digester relief, that the weakly acid or carboxylic type resin cannot be used effectively. On the other hand a strong solution of SO_2 can be used to regenerate or reconvert the sulfonic resin to the hydrogen form and thus remove a substantial portion of the sodium or other base ions absorbed on the column.

What I claim is:

1. A method of recovering base ions selected from the group consisting of sodium and ammonium ions from waste liquor produced in a neutral sulfite pulping process and of producing fresh neutral sulfite cooking liquor containing said base ions which comprises passing said waste liquor successively through a plurality of bodies of cation exchange resins in the hydrogen form, one of said bodies being a carboxylic resin and the other a sulfonic resin, said waste liquor being passed firstly through said body of carboxylic resin and the effluent therefrom being passed through said body of sulfonic resin, and subsequently passing a solution of available sulfurous acid firstly through said body of sulfonic resin and then through said body of carboxylic resin and collecting the effluent from the latter to provide fresh cooking liquor.

2. A method according to claim 1 in which said solution having available sulfurous acid is passed through said bodies of resin in the opposite direction from that in which said waste liquor is passed through said bodies of resin.

3. A method according to claim 1 in which the alternate passage of the waste liquor and of said solution is so regulated that the resins in said bodies are only partially converted from the hydrogen form to the base form and are only partially converted from the base form to the hydrogen form upon the successive passage of quantities of said waste liquor and of said solution, said carboxylic resin being alternately converted to a form in which from 90 to 100% is in the hydrogen form to one in which from 40 to 80% is in the hydrogen form with the balance in each instance being in the base form, and said sulfonic resin being alternately converted to a form in which from 25 to 60% is in the hydrogen form to one in which from 0 to 20% is in the hydrogen form with the balance in each instance being in the base form.

4. A method of recovering base ions selected from the group consisting of sodium and ammonium ions from waste liquor produced in a sulfite pulping process and of producing fresh sulfite cooking liquor containing said base ions which comprises passing said waste liquor successively through a plurality of bodies of cation exchange resins in the hydrogen form, one of said bodies being a carboxylic resin and the other a sulfonic resin, said waste liquor being passed firstly through said body of carboxylic resin and the effluent therefrom being passed through said body of sulfonic resin, and subsequently passing a solution of available sulfurous acid firstly through said body of sulfonic resin and then through said body of carboxylic resin and collecting the effluent from the latter to provide fresh cooking liquor.

5. A method of recovering base ions selected from the group consisting of sodium and ammonium ions from waste liquor produced in a sulfite pulping process and of producing fresh sulfite cooking liquor containing said base ions which comprises passing successively through a plurality of bodies of cation exchange resins in the hydrogen form a material selected from the group consisting of said waste liquor and a liquor derived from said waste liquor by the concentration thereof with subsequent smelting of the concentrated liquor and the dissolution of the smelt, one of said bodies being a carboxylic resin and the other a sulfonic resin, said material being passed firstly through said body of carboxylic resin and the effluent therefrom being passed through said body of sulfonic resin, and subsequently passing a solution of available sulfurous acid firstly through said body of sul-

fonic resin and then through said body of carboxylic resin and collecting the effluent from the latter to provide fresh cooking liquor.

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