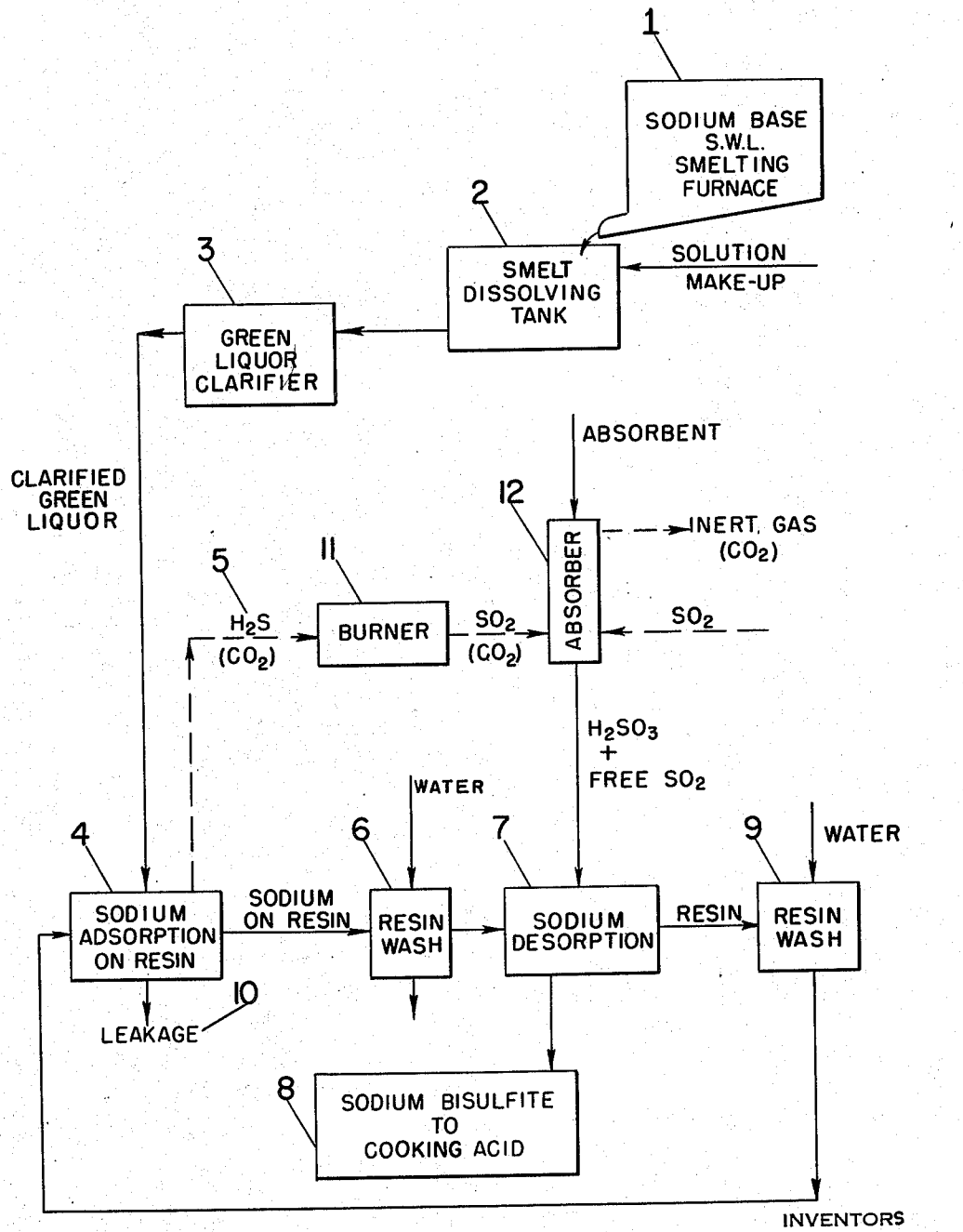
Oct. 20, 1953 K. R. GRAY ET AL 2,656,244

PROCESS OF RECOVERING CHEMICALS FROM SMELTS OBTAINED IN PULPING OPERATION

Filed July 15, 1950



INVENTORS

KENNETH RUSSELL GRAY & HARTZELL LANCE CROSBY

BY

Pennie, Edmonds, Morton & Barrows

ATTORNEYS

Patented Oct. 20, 1953

2,656,244

UNITED STATES PATENT OFFICE

2,656,244

PROCESS OF RECOVERING CHEMICALS FROM SMELTS OBTAINED IN PULPING OPERATION

Kenneth Russell Gray and Hartzell Lance Crosby, Shelton, Wash., assignors to Rayonier Incorporated, Shelton, Wash., a corporation of Delaware

Application July 15, 1950, Serial No. 174,103

9 Claims. (Cl. 23—48)

1

This invention relates to the production of pulp and provides improvements in the recovery, preparation and use of chemicals used therein. The invention is particularly concerned with the treatment and utilization of the smelts obtained in pulping operations.

In the acid sulfite pulping process, for example, a lignocellulose material is generally cooked in a solution of sulfurous acid, part of the sulfurous acid being combined as bisulfite. The cation combined thus with the bisulfite ion is known as the pulping base. In the past, for economic reasons, this pulping base has almost universally been calcium.

On the other hand, in the alkaline pulping industries, the desirability of the use of sodium as a pulping base has long been recognized. Advantage is taken of the high solubility properties and the economic recovery of the base for reuse.

For over a century, it has been standard practice in the alkaline pulping industries to recover the base (sodium) by combusting the organic matter. Recent improvements in equipment design along with higher fuel costs have resulted in considerable economic advantage for heat recovery in modern installations.

The sulfite pulping process was originally developed using soda-base liquors. However, commercial use of soda-base cooking liquor was not economically practical since no satisfactory process was available for the conversion to usable form of the soda salts recoverable by combusting the liquor. Therefore, as the sulfite process became employed on a wide scale, manufacturers turned to use of calcium for the preparation of cooking acid, since the limestone was inexpensive and the waste liquor could therefore be discarded.

In recent years, disposal of waste sulfite liquors by discharging in streams and inlets has met with increased opposition. Furthermore, economic considerations such as the increased cost of fuel have accentuated the desirability of recovering heat and pulping chemicals in a manner similar to that practiced in alkaline pulping.

Many attempts have been made to evaporate calcium-base waste liquor for subsequent burning. In the United States, such attempts have never come to commercial practice largely because of difficulties of scale formation during

2

evaporation and the formation of an infusible ash on combustion.

In Europe, these difficulties have been overcome sufficiently to permit evaporation and combustion of calcium-base waste liquor. However, only heat is recovered because in the combustion process, calcium sulfate is formed from which the original cooking chemicals are not practically recoverable. These difficulties regarding evaporation and burning of waste liquor may be eliminated by employing sodium as a base.

When either kraft or soda-base sulfite waste liquor is evaporated and burned, a smelt is produced containing various quantities of sodium sulfide, sodium carbonate, and sodium sulfate. The smelt so produced is not directly suitable as a pulping chemical in either type of process. In the kraft industry, conversion of the smelt into usable form is relatively simple involving essentially the conversion of sodium carbonate in the smelt to sodium hydroxide.

For the production of soda-base sulfite cooking liquor, conversion of the smelt to usable form has been a problem not heretofore solved in a practical manner. Conversion of smelt to cooking liquor cannot be effected directly since treatment of the smelt directly with sulfur dioxide would convert a portion of the sodium sulfide to polythionates, thiosulfate, free sulfur, etc., all of which interfere with the acid sulfite pulping process.

Development of such conversion processes would give the following great advantages:

1. It would be practical to practice soda-base sulfite pulping.

2. Heat equivalent to a large amount of oil would be obtained, since the organic matter in the waste liquor will provide 8–9000 B. t. u. per lb. dry organic solids or considerably in excess of the heat required for the multiple effect evaporation of the liquor to a concentration suitable for burning.

3. Effluent liquors requiring disposal would be practically eliminated.

4. Recovery of chemicals for re-use would provide operating cost advantages.

Our invention provides a simple, practical process for converting a smelt containing sodium sulfide into sodium bisulfite either free from, or hav-

ing a minimum quantity of, objectionable by-products.

This invention is based on our discovery of the treatment of soda salts of weakly acidic volatile acids with certain cation exchange resins for the adsorption of sodium on the resin, the release of the weak acid, and the regeneration of sodium bisulfite by treating the resin with sulfurous acid. The general applicability of our invention is described and claimed in our copending application Serial Number 174,102, filed July 15, 1950.

Our present process utilizes the important conjoint steps which we have discovered comprising treating aqueous solutions of soda salts of weakly acidic volatile acids such as CO_2 and H_2S with a cation exchange resin having active exchange centers in hydrogen form which are substantially less acidic than sulfurous acid, resulting in the adsorption of the sodium on the resin with the liberation of the weak volatile acid, and the treatment of the resin with sulfurous acid to form sodium bisulfite. The resin is accordingly regenerated for further use.

In one preferred application, the sulfur dioxide used for treating the resin containing sodium is obtained at least in part by the oxidation of the hydrogen sulfide evolved in the above treatment.

Where the solution containing the sodium salt of weakly acidic volatile acids also contains the sodium salts of relatively nonvolatile, strong acids, the resin treatment will adsorb the sodium component of only the weakly acidic volatile acids. Thus, since the weakly acidic volatile acids are liberated from the solution in gaseous form and the sodium is adsorbed on the resin, a complete separation of the sodium salts of the weakly acidic volatile acids from the sodium salts of the relatively nonvolatile, strong acids can be effected.

Among the resins which we have found particularly applicable in our process are those containing carboxylic acid or phenolic hydroxyl exchange centers, or both, and in particular, the newer synthetic organic exchange resins containing these groups exclusively and which are characterized by high adsorptive capacities. A number of resins of this type are at present available. The carboxylic acid type resins are especially desirable. One such resin which we have found particularly suitable is sold under the trade name of "Amberlite IRC–50."

We have found that the process may very advantageously be conducted at elevated temperature, as for example, 50–100° C., whereby the effective capacity of the resin is not only materially increased due to the temperature effect but due to the reduced solubility of the evolved volatile acids. Thus, one reaction product is effectively removed from the solution enabling very rapid approach to equilibrium conditions and facilitating adsorption of the soda. Removal of the volatile acid may also be further facilitated by carrying out this phase under vacuum.

Following the adsorption step, the resin is washed in a conventional manner and the adsorbed soda removed by a treatment with sulfurous acid solution. In place of sulfurous acid solution, the resin containing sodium may be treated with sulfurous acid formed in situ by passing sulfur dioxide containing gases in contact with the wet resin.

It is understood that, depending on the characteristics of the installation, the sodium adsorption and/or desorption may be carried out in more than one step.

It is a desirable feature of our process that many impurities present in the original solution (e. g. chlorides, sulfates, thiosulfates, etc.) remain in the liquor drained from the resin following the adsorption step and therefore the regenerated solution or product liquor is recovered as a high quality material.

The sulfide content of the influent solution is largely released as hydrogen sulfide during the soda adsorption stage. With influence solutions of substantial sulfide content the hydrogen sulfide is evolved in substantial concentration and may be readily and practically burned to sulfur dioxide free from undesirable by-products, whereupon it may be used in the process if desired for removal of the sodium from the resin as sodium bisulfite.

The solution, from which all or a portion of the soda has been removed, is drained from the resin at the completion of the adsorption step. This said effluent solution has been termed by us the "leakage" and the term "leakage" is hereinafter used in the specification in this sense.

In one method of applying our process, where only salts of weakly acidic volatile acids are present, the ratio of the amount of resin used in the treatment to the amount of soda salts of the weakly acidic volatile acids is such that substantially all of the soda of the influent solution is adsorbed on the resin and substantially all of the volatile acids are liberated in gaseous form. The leakage from this process, containing substantially no sodium ions, may be readily stripped of any remaining traces of volatile hydrogen sulfide and may therefore be reused as water in the process or discarded with no attendant waste disposal problem.

In another method of applying our process, the sodium containing solution influent to the resin treatment contains, in addition to the soda salt of weakly acidic volatile acids, other soda salts, such as soda salts of strong acids, which are not decomposed in the exchange reaction and therefore remain in the leakage.

By limiting the ratio of influent liquor to resin, relatively complete removal of the soda from the salts of the weakly acidic volatile acids may be achieved, in which case the leakage contains largely the sodium salts of the relatively nonvolatile acids and may be either recycled in the process, treated for recovery of the inactive soda values, or discarded.

Where the liquor influent to the resin contains sodium salts of the weakly acidic volatile acids substantially in excess of the effective capacity of the resin, and in addition sodium salts of relatively nonvolatile acids, the leakage will contain substantially the total amount of the sodium salts of the relatively nonvolatile acids as well as the unadsorbed portion of the soda salts of the weakly acidic volatile acids. Operation in this manner provides a very high soda ion concentration in the influent solution throughout the reaction stage, thereby resulting in exceptionally high effective capacities and efficient use of the resin. The leakage from such operation would contain considerable soda values and could be recycled, treated for further soda recovery, or used elsewhere in the process.

The accompanying drawing illustrates diagrammatically by flow sheet an operation embodying the invention.

Soda-base sulfite waste liquor recovered as an

effluent from the digestion of cellulosic substances in soda-base acid sulfite cooking liquor, is concentrated to at least 50% total solids content in conventional multiple-effect evaporators and fired to a smelting type recovery furnace (1). This furnace may be similar to the conventional units now used in the kraft and soda pulp mills throughout the industry. When operated under reducing conditions in the smelting zone (e. g., with high temperatures and limited excess air), the furnace will generate steam and yield a "smelt" of fused soda salts. This smelt flows from the furnace and may, for example, be quenched or otherwise dissolved (2) in water or some suitable effluent solution from the process to yield a characteristic "green liquor" containing essentially sodium sulfide with smaller amounts of sodium carbonate, sodium sulfate and sodium thiosulfate. Following clarification in conventional clarification equipment, the green liquor is ready for treatment for the recovery of soda and production of sulfite cooking acid.

In one adaptation of the invention, a suitable resin (for example, the weakly-acidic carboxylic-acid type) in hydrogen form is contacted in a bed with the proper amount of smelt solution. This may be accomplished in a number of ways, as for example by passing the solution through a bed of the resin or by adding the resin to the solution either batchwise or in a continuous manner, later separating the resin from the solution by mechanical means. The conditions of this treatment are not critical in any way with regard to time, temperature, or solution concentration; however a high solution concentration (100 grams equivalent Na_2O per liter) speeds the reaction and permits a high resin capacity. Since adsorption of the soda (4) is accompanied by the spontaneous evolution of the corresponding free acids, H_2S and H_2CO_3 (5), the reaction may conveniently and advantageously be carried out at an elevated temperature of 60–90° C., which approximates the temperature of the green liquor from the clarifiers. This elevated temperature reduces the solubility of the volatile product gases, thereby accelerating the reaction and improving the effective capacity of the resin.

Where the ratio of soda to resin is such that the capacity of the resin is not exceeded, substantially complete removal of the soda present as sulfide and carbonate can be accomplished and this represents the preferred method of operation.

However, it may be noted that use of green liquor containing sodium in excess of the capacity of the resin increases the driving force and the effective capacity of the resin. Under some conditions, it may be desirable to operate in this manner, returning the "leakage" containing unreacted sulfide and carbonate to the process for dissolving additional smelt.

The resin containing the adsorbed sodium is washed by displacement (6) to remove excess smelt solution. The washed resin is then treated with an excess of sulfurous acid solution which effects a complete regeneration of the resin and desorption of the soda (7) to form an effluent containing sodium bisulfite and free sulfurous acid (8). This solution may be used directly as cooking acid or it may be diluted if desired or fortified with additional free SO_2.

Subjecting the resin to a brief wash to remove residual acid (9) completes the cycle and leaves the resin ready for reuse. Steps (5), (6), (7) and (9) represent steps in the cyclic treatment of a single batch of resin.

The treatment of the leakage from the soda adsorption step (10) is largely dictated by its composition which, in turn, is a function of the pulping process, the furnace operation, and the ion exchange cycle. In general, the main components will be sodium sulfate, sodium thiosulfate, and traces of dissolved gases. If the mill uses salt water floated logs, chloride will also be a major constituent. The dissolved gases may be very readily removed by stripping, if desired; however, due to the limited solubility, the amount of gas present in the leakage is very small. If the inactive salts in the leakage represent an appreciable soda value, economic considerations will necessitate their being retained in the system. Where the nature and amount of the salts are such that no detrimental effects will be incurred in the cooking cycle, the leakage may be used to make up sulfurous acid solution and used as regenerant for the resin or may be simply added to the cooking acid as a diluent. In such a case sulfur dioxide gas, either pure or diluted (e. g., burner gas), may be passed directly into the mass of resin and smelt solution from which the sulfide has been eliminated, thereby forming sulfurous acid in situ, effecting regeneration of the resin by desorption of the sodium, and forming a sodium bisulfite solution which is simply drained from the resin and used in the preparation of cooking acid.

The sulfate and traces of thiosulfate carried into the cooking acid would be returned to the furnace in the waste liquor from the cook, where they would be largely reduced to sulfide during the smelting operation, thereby preventing an accumulation of these salts in the system.

Recovery of the soda values in the leakage, consisting in large part of sodium salts of strong and non-volatile acids, may also be accomplished either by evaporation of the excess water and return of the concentrated solution to the furnace or by treatment with an ion exchange resin containing strongly acidic groups and capable of adsorbing the sodium from the neutral salts.

Returning the leakage to the smelt dissolving tank is practical, especially where the residual salt concentration is low. However, this would result in an accumulation of the inactive salts in the cycle and would necessitate provision for the removal of a portion of these salts each cycle in order to prevent precipitation of soda compounds due to concentrations exceeding the solubility limits.

The gas evolved during the soda adsorption step (5) consists of H_2S and CO_2 in mol ratio substantially equal to the mol ratio of sulfide to carbonate in the green liquor. Due to the high ratio of sulfur to soda in the digestion liquor used in the sulfite process, the ratio of sulfide to carbonate in the smelt may be on the order of 3:1 to 8:1 depending on furnace operation. It can be seen that the evolved gases are preponderantly H_2S with the practical advantage that they are in sufficiently high concentration to be readily burned (11), resulting in the production of SO_2 which may be adsorbed (12) to produce a portion of the sulfurous acid required for removal of sodium from the resin (7).

The absorbent for this SO_2 may be water, or more conveniently one of the effluents from the exchange cycle may be used in order to maintain a substantially closed system, thereby reducing soda or sulfur losses. Thus, the absorbent solu-

tion might be the leakage, or one of the wash effluents.

Washing may be carried out in a manner familiar to the art whereby a strong and a weak fraction is recovered, the strong fraction being added to the effluent from the preceding stage and the weak fraction being stored for the first wash liquor of the subsequent cycle.

The example outlined above is only intended as an illustration of one application and it is obvious that the invention may be applied to a variety of pulping operations. Many such operations proposed in the past have not heretofore been practical but are now rendered economically feasible by use of the present invention.

As an example of use in another pulping operation, the invention may be applied to a pulping sequence wherein lignocellulosic material is treated in one stage with a sodium base acid sulfite solution and in another stage with an alkaline solution. The waste liquors from these treatments, containing organic matter, sodium and sulfur, could be combined, evaporated to 45% to 75% total solids and burned in a furnace similar to that used in the alkaline pulping industry, to generate steam and recover a fused mass of soda chemicals. This smelt flows from the furnace and is dissolved in water or a process effluent to produce a characteristic green liquor containing sodium sulfide and sodium carbonate with smaller amounts of other soda chemicals.

Clarification of the green liquor is carried out in conventional clarification equipment, whereupon all or a portion of the liquor is diverted to the ion exchange plant. This plant is operated according to the process disclosed by us to remove sufficient sodium from the green liquor to supply the soda base requirements of the acid sulfite treatment step. Hydrogen sulfide and carbon dioxide are evolved during the resin treatment, and sodium is adsorbed on the resin. The leakage, plus the balance of the liquor if only a portion was treated in the ion exchange plant, is treated by a conventional causticizing process to create the desired alkaline liquor for pulp preparation. The resin is washed, and treated with a sulfurous acid solution to regenerate the resin and to produce sodium bisulfite for use in the acid sulfite treatment of lignocellulose. As has been mentioned previously in this specification, the sulfur dioxide to prepare said sulfurous acid solution may be obtained at least in part from oxidation of the hydrogen sulfide evolved in the process. Where the concentration of sulfur dioxide in the product gases from the oxidation is low, a relatively concentrated gas can be obtained by absorbing the sulfur dioxide in a suitable solvent (e. g., water, ammonium sulfite solution or an alkanolamine) and subsequently liberating it in concentrated form by heat.

Certain pulping applications require use of neutral sodium sulfite rather than sodium bisulfite. These include the so-called neutral sulfite process as well as processes using strongly alkaline cooking liquors. Examples of such liquors would include mixtures essentially consisting of

$NaOH+Na_2SO_3$, $NaOH+Na_2S+Na_2SO_3$
$Na_2CO_3+Na_2SO_3$, $Na_2CO_3+Na_2S+Na_2SO_3$

and other combinations.

Neutral sodium sulfite can be conveniently prepared for various uses by reacting sodium bisulfite recovered in the manner heretofore described with sodium carbonate or bicarbonate at an elevated temperature. Caustic soda may also obviously be used for reacting with the sodium bisulfite to produce sodium sulfite.

Sodium bicarbonate or caustic soda for such use may be obtained in a modification of the invention. In such modification the resin containing adsorbed sodium is regenerated at least in part with carbonic acid, whereupon sodium salts of carbonic acid would be formed which could be used as such or converted to caustic soda in a causticizing operation. Depending upon the products desired a split regeneration first with carbonic acid to the desired degree, then with sulfurous acid to complete the regeneration may be used. By controlling the regeneration to give sodium bicarbonate and sodium bisulfite in substantially equimolecular quantities, the resulting product solutions may be mixed at an elevated temperature whereupon carbon dioxide is evolved and a solution of normal sodium sulfite substantially free from bicarbonate is formed.

In order to utilize the maximum effective capacity of the resin, it may be desirable to regenerate with solutions containing carbon dioxide or sulfur dioxide in excess of the theoretically required amount. Following regeneration the resulting effluents may be stripped of the excess volatile constituent to produce solutions substantially free of excess regenerant.

In one modification our process may be advantageously applied to the preparation of pure chemicals from naturally occurring mineral deposits or brines containing sodium salts of weakly acidic volatile acids. An analysis of one such deposit is shown below.

Analysis of natural brine from Soap Lake, Washington

	Weight per cent of T. S.
Sodium carbonate	33.9
Sodium bicarbonate	16.2
Sodium sulfate	26.6
Sodium chloride	20.1
Minor constituents	3.2
Total	100.0

Whereas separation of these salts by crystallization techniques would present considerable difficulty, the carbonate and bicarbonate fraction of such a brine can be readily and simply recovered as sodium bisulfite by application of our ion exchange process.

In another modification of our process sodium sulfate may be smelted with coal or other carbonaceous matter to yield a smelt containing sodium sulfide and carbonate. This may be readily converted to sodium bisulfite by our process in a manner similar to the preparation of sodium bisulfite from the smelt resulting from the combustion of soda-base sulfite waste liquor. In that our process effects a purification, extremely impure sodium sulfate may be used as a raw material. In fact, naturally occurring sodium sulfate or chemical wastes containing sodium sulfate may be used even in the presence of considerable contaminants such as chlorides, carbonates, etc.

Ion exchange resins are in general porous, cross-linked polymeric materials which contain ionizable groups throughout the resin which are capable of exchanging one ion for another. They may thus be considered to be solid gel structures of an ionic nature.

The process of the invention is not limited to

any particular manner of preparation of the carboxylic acid or phenolic hydroxyl type ion exchange resins used. Some methods whereby satisfactory weakly acidic resins may be prepared follow.

Carboxylic acid type resins may be prepared by polymerizing or co-polymerizing unsaturated organic acids or their anhydrides under conditions whereby cross-linked polymers are formed. Alternatively, esters of unsaturated organic acids may be polymerized to form a cross-linked resin and later saponified. Again, non-cross-linked alkali-soluble polymers containing carboxyl groups may be subjected to a cross-linking reaction to prepare an insoluble ion exchange resin. Again, carboxylic acid groups may be introduced into natural polymers not already containing these groups. In such cases, where necessary to obtain insolubility, a prior, concurrent, or subsequent cross-linking treatment would be effected. Introduction of carboxyl groups could be effected by such means as substitution of carboxy-alkyl groups or by partial oxidation of the original structure.

Phenolic hydroxyl type ion exchange resins may be prepared by polymerizing phenols (preferably polyphenols) to give a porous cross-linked polymer, as, for example, by use of suitable amounts of formaldehyde. Naturally occurring tannins provide an economically attractive source of polyphenols for this purpose. Alternatively, phenolic hydroxyl groups may be produced in naturally occurring polymeric materials not containing appreciable amounts of this group, by such means as hydrolysis of phenol-ether or ester groups in the original molecule. Again, in such cases where necessary to obtain insolubility, prior, concurrent, or subsequent cross-linking will be effected.

Ion exchange resins containing both carboxyl and phenolic hydroxyl groups may be prepared by polymerizing simple molecules containing both carboxylic acid and phenolic hydroxyl groups. Alternatively, such resins may be prepared by subjecting polymeric materials containing phenolic hydroxyls as the only exchange groups to procedures whereby carboxylic acid groups are introduced in addition to the phenolic hydroxyl groups. Here, also, where necessary to obtain insolubility, prior, concurrent, or subsequent cross-linking will be effected.

Examples illustrating the process of the invention as well as the preparation of some weakly acidic resins are given below.

EXAMPLE I

Ninety ml. of styrene, 60 ml. of a divinylbenzene solution containing 20–25% divinylbenzene dissolved in other aromatic hydrocarbons, 100 gms. of maleic anhydride, and 50 ml. of acetone were heated on a steam bath for a period of two hours. Temperature in the mixture rose to a maximum of 107° C. and dropped to 90° C. at the end of the two hour period. The product was then heated in an oven at 135° C. for three hours. It was then washed thoroughly with acetone, soaked for 18 hours in 5% NaOH and then thoroughly washed with water and dried. Yield of product was 121 grams.

Three-hundred ml. of this wet resin in hydrogen form was slurried with 100 ml. of solution containing 76.5 gm. sodium per liter, 80% of which was present as sulfide and carbonate; the balance being present as sulfate, chloride, thiosulfate and sulfite. The reaction was allowed to proceed for 15 minutes at atmospheric pressure and at 80° C., during which time hydrogen sulfide and carbon dioxide were spontaneously evolved from the solution and sodium was adsorbed on the resin. The resin was then separated from the solution, washed, and treated with 500 ml. of sulfurous acid containing 30 grams sulfur dioxide for 15 minutes at 25° C. and atmospheric pressure. The product solution containing all the sodium formerly adsorbed on the resin was drained off, and the resin was washed, whereupon it was ready for re-use. In this experiment 6.9 gm. sodium was adsorbed by the 300 ml. of resin and was regenerated by means of sulfurous acid.

EXAMPLE II

Using automatic ion exchange equipment, 500 repeated cycles were carried out with the following average results: 4000 ml. wet carboxylic acid type cation exchange resin (sold commercially under the trade name of "Amberlite IRC–50") in hydrogen state was treated with 3.78 liters of solution containing 110 gm. Na_2O per liter and having the following composition (expressed as mol per cent Na_2O): Na_2S 65%, Na_2Co_3 15%, Na_2SO_4 15%, NaCl 3%, $Na_2S_2O_3$ 1.6%, Na_2SO_3 0.4%. This treatment was conducted at 50° C. for 15 minutes at atmospheric pressure during which period H_2S and Co_2 were spontaneously evolved and 210 gm. sodium was adsorbed on the resin. (This represents adsorption of 68% of the total influent sodium or 85% of the sodium initially present as salts of weak volatile acids.) Following a brief wash, the resin was treated with sulfurous acid containing 25 gm. SO_2 per liter to produce a solution of sodium bisulfite at a concentration of 7.4 grams sodium per liter and containing all of the sodium formerly adsorbed on the resin (210 grams).

At the completion of every 100 cycles the sodium adsorption capacity of the resin was measured and at the completion of 500 cycles the total resin volume was measured and the resin was screened. No loss of sodium adsorption capacity had occurred and no measurable decrease in resin volume or appreciable change in screen analysis was found.

EXAMPLE III

1500 grams of quebracho tannin were dissolved in 1500 ml. of water in an autoclave and 609 ml. of formalin and 15 ml. of concentrated hydrochloric acid were added. The mixture was then heated with a steam jacket with a steam pressure of 115 lbs./sq. in. in the jacket. Heating was continued for three hours, during which time the temperature reached 135° C. in the autoclave. The mass was then removed from the autoclave, dried at low temperature and heated at 105° C. for a total of 36 hours. The product was then ground and screened to remove fines.

200 ml. of this wet resin in hydrogen form was slurried with 200 ml. of solution containing 100 gm. sodium per liter, 85% of which was present as sulfide and carbonate; the balance being present as sulfate, chloride, thiosulfate and sulfite. The reaction was allowed to proceed for 15 minutes at atmospheric pressure and at the desired temperature, during which time hydrogen sulfide and carbon dioxide were spontaneously evolved from the solution and sodium was adsorbed on the resin. The resin was then separated from the solution, washed, and treated with 500 ml. of sulfurous acid containing 30 grams sulfur

dioxide for 15 minutes at 25° C. and atmospheric pressure. The product solution, containing all the sodium formerly adsorbed on the resin, was drained off and the resin was washed, whereupon it was ready for re-use. Typical results of such an experiment are as follows:

Resin	Temperature of Sodium Adsorption, °C.	Sodium Adsorbed by 100 ml. Wet Regenerated Resin, gms.	Sodium Recovered by Regeneration with Sulfurous Acid, gms.
Phenolic Hydroxyl Resin (prepared as described above)	26	2.1	2.16
	82	2.8	2.92

We claim:

1. In the preparation of wood pulps, the process for recovering chemicals which comprises combusting waste liquor from the alkaline treatment of sulfite digested pulp to yield a smelt containing a sodium salt of a weakly acidic volatile acid of the group consisting of hydrogen sulfide and carbonic acid, treating a solution of said smelt with a cation exchange resin having active exchange centers in hydrogen form which are substantially less acidic than sulfur dioxide and evolving a substantial portion of said volatile acids in gaseous form and adsorbing sodium on the resin, treating said resin containing adsorbed sodium with sulfurous acid to form a solution containing sodium bisulfite suitable for use in the acid sulfite digestion of wood, and returning the sodium bisulfite to the pulping operation.

2. In the process of claim 1, treating the resin containing the adsorbed sodium with sulfurous acid to form a solution containing sodium bisulfite suitable for use in the sulfite digestion of wood.

3. In the preparation of wood pulp, the process for recovering chemicals which comprises combusting combined waste liquors from successive sulfite and alkaline treatments of wood to yield a smelt containing a sodium salt of a weakly acidic volatile acid of the group consisting of hydrogen sulfide and carbonic acid, treating a solution of said smelt with a cation exchange resin having active exchange centers in hydrogen form which are substantially less acidic than sulfur dioxide and evolving a substantial portion of said voltaile acids in gaseous form and adsorbing sodium on the resin, treating said resin containing adsorbed sodium with sulfurous acid to form a solution containing sodium bisulfite suitable for use in the sulfite treatment, and returning the sodium bisulfite to the pulping operation.

4. In the preparation of wood pulp, the process for recovering chemicals which comprises combusting waste liquor from a sulfite digestion of wood to yield a smelt containing sodium salts of weakly acidic volatile acids including hydrogen sulfide, treating a solution of said smelt with a cation exchange resin having active exchange centers in hydrogen form which are substantially less acidic than sulfur dioxide and evolving a substantial portion of said volatile acids as a gas and adsorbing sodium on the resin, oxidizing the hydrogen sulfide content of said gas to form sulfur dioxide, treating said resin containing adsorbed sodium with sulfurous acid derived at least in part from the oxidation of hydrogen sulfide to form a solution containing sodium bisulfite suitable for use in the sulfite digestion of wood, and returning the sodium bisulfite to the pulping operation.

5. The process of claim 4 in which the waste liquor is from an alkaline treatment of sulfite digested pulp.

6. The process of claim 4 in which the waste liquor is from successive sulfite and alkaline treatments of wood.

7. The process of claim 4 in which the resin has carboxylic acid-type exchange centers in hydrogen form.

8. The process of claim 4 in which the resin has phenolic hydroxyl exchange centers in hydrogen form.

9. The process of claim 4 in which the resin has in hydrogen form both carboxylic acid-type and phenolic hydroxyl exchange centers.

KENNETH RUSSELL GRAY.
HARTZELL LANCE CROSBY.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,545,522	Richter	July 14, 1925
1,638,492	Laury	Aug. 9, 1927
2,104,501	Adams et al.	Jan. 4, 1938
2,409,861	Hunter et al.	Oct. 22, 1946

FOREIGN PATENTS

Number	Country	Date
118,486	Australia	May 4, 1944
521,207	Great Britain	May 15, 1940

OTHER REFERENCES

Ion Exchange in Waste Treatment, Ind. and Eng. Chem. vol. 41, No. 3 (Mar. 1949), pages 448 to 451.