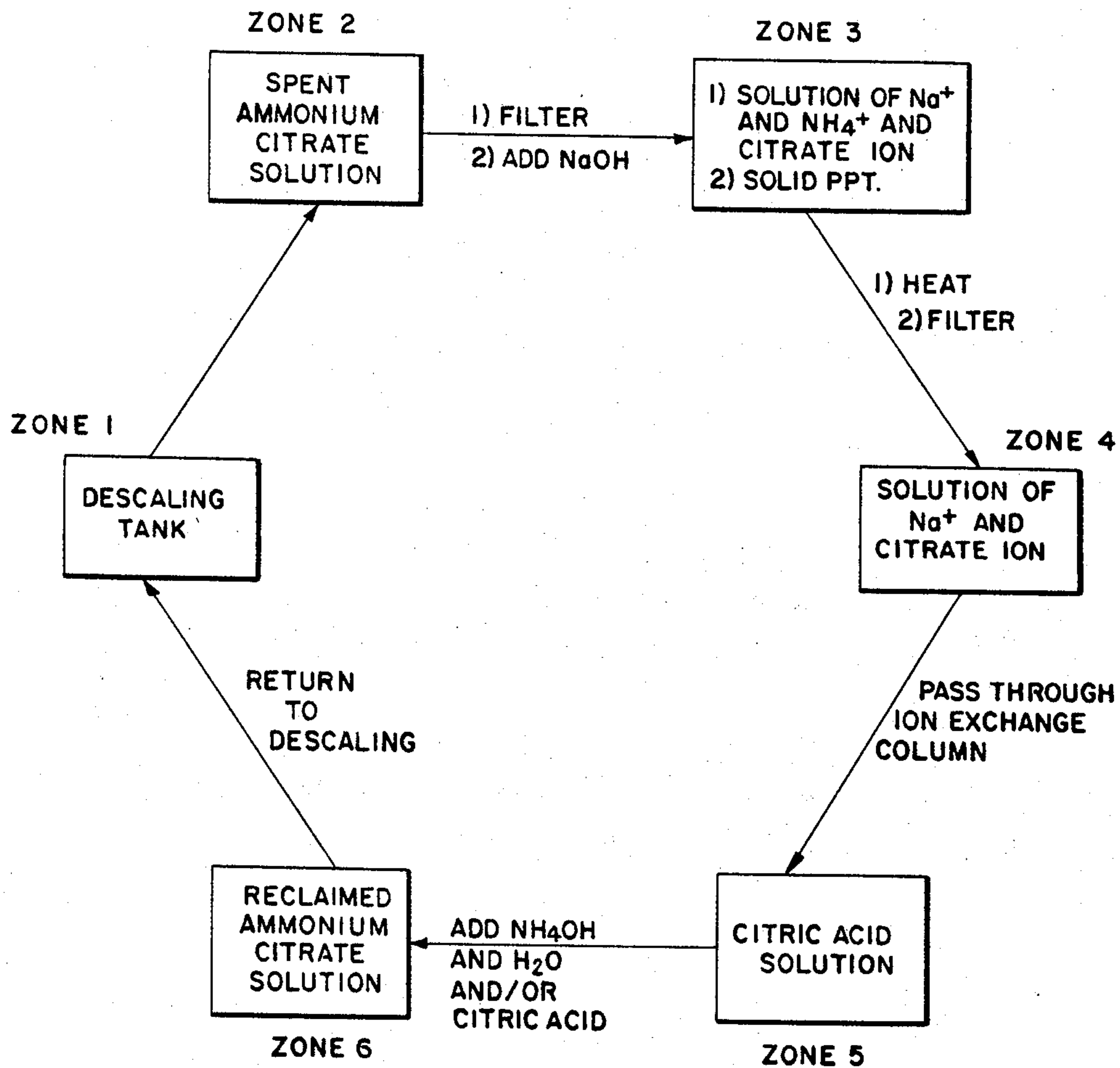


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ELECTROLYTICALLY DESCALING STEEL  
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1

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## PROCESS FOR RECLAIMING SPENT ELECTROLYTES USED FOR ELECTROLYTICALLY DESCALING STEEL

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### ABSTRACT OF THE DISCLOSURE

Process for reclaiming a spent aqueous electrolyte solution of an organic chelating agent recovered from the electrolytic descaling of steel surfaces. Process comprises raising the pH of the spent electrolyte to at least about 10.5 with a water soluble hydroxide, separating precipitated solids therefrom and then reducing the pH of the resultant solution to at least 7 with a cation exchange resin.

The present invention relates to the production of substantially pure electrolyte for use in electrolytic descaling of metals by a process which involves the reclamation of spent electrolyte resulting from said electrolytic descaling of metals.

Copending application Ser. No. 452,055, filed Apr. 30, 1965, by Bernard J. Freedman, Richard A. Georgetti and William R. Tedeschi, and assigned to the same assignee as the instant application, is for a Process for Electrolytic Descaling, and describes a novel electrolytic process for removing scale from metal surfaces using specific electrolytes. It is intended to incorporate herein by reference the disclosure of said copending application in its entirety.

The electrolytes disclosed in the aforementioned copending application are aqueous solutions of a salt of a nitrogen base or of an alkali metal hydroxide with an organic acid, the organic acid being such that a molecule of the acid can bind a metal ion simultaneously through two or more positions so that multiple rings can be formed, or in other words can react with metal ions to form soluble complexes, such acids conventionally known as chelating agents. These electrolytic salt solutions have a pH of about 3 to 7 when a salt forming nitrogen base is used and a pH of about 3 to 6 when a salt forming alkali metal hydroxide is used. A preferred pH when a salt forming nitrogen base is used is 5 while a preferred pH when a salt forming alkali metal hydroxide is employed is 4. Suitable organic acids include gluconic acid, tartaric acid, diglycolic acid and especially glycolic acid and citric acid. Citric acid is particularly preferred. The term "nitrogen base" as used above includes ammonium hydroxide and organic amines which give an alkaline reaction in aqueous solution and form salts with acids. Examples of organic amines are alkanol amines such as ethanolamine and alkyl amines as ethylamine and triethylamine. As the nitrogen base ammonium hydroxide is particularly advantageous. Particularly effective alkali metal hydroxides are solid hydroxide and potassium hydroxide.

Other components can be present as desired in the electrolytic solutions. These include nonionic surfactants, ionic surfactants, corrosion inhibitors, strong electrolytic ionic inorganic salts and the like. The concentration of the acid component in the electrolyte should be at least about 5 percent and may be as high as about 50 percent with a preferred percentage of about 25 to about 35 percent, the percent expressed in grams of acid component

2

per liter of solutions or in any other units corresponding to the same ratio. A 28 percent acid component when citric acid is used has been found to be especially suitable. Such a solution can be prepared by dissolving 280 grams of citric acid in water, simultaneously adjusting the volume of the solution to one liter and the pH to the desired value by addition of water and the appropriate base.

The electrolytic solutions having achieved a desired descaling in the electrolytic process of said copending application are conventionally in what is called a spent state, the effectiveness of the salt solutions having been reduced because of the electrolytic descaling. This spent state is largely due to the fact that the scale on the metal surface has reacted with the acid component of the electrolyte and as a result of a sequestering or chelating action occurring between the undesirable metal component of the scale and acid component, has formed a complex. The term "spent" as used herein is not intended to encompass merely an electrolyte which has been rendered totally ineffective for the electrolytic descaling process of the aforementioned application but rather includes an electrolyte whose effectiveness has been rendered less than optimum during the electrolytic descaling process of said copending application.

It is highly desirable to develop an efficient process for treating either continuously or batchwise the spent solutions of said copending application in order to remove the chelated metal from the acid component and produce fresh electrolyte which could then be reused in the electrolytic descaling process. The acid component of the electrolyte is expensive and, accordingly in many instances, in the absence of an efficient reclamation process, economics alone will dictate the tolerance of limited amounts of scale in preference to its removal. Moreover, aside from economics, an efficient reclamation process is highly advantageous since it allows for a continuous electrolytic descaling process without interruption of the process because of a need for fresh electrolyte. With an efficient reclamation process, a spent electrolyte can continuously be made to leave the descaling tank, undergo a reclamation and the resultant electrolyte be returned to the descaling tank for reuse in the electrolytic descaling process.

An added advantage in the reclamation of spent electrolyte is the removal of any free acid from the waste stream, i.e. the elimination of the disposal problem of waste acid solutions normally encountered in present descaling processes.

Various processes for reclaiming spent electrolytic descaling solutions of said copending application have been attempted but all prior attempts, both from a technical and economic aspect, have proven impractical, especially in the treatment of large quantities of such spent electrolyte. To illustrate, treatment of a spent ammonium citrate solution with barium chloride resulted in a solid barium citrate which on acidification with sulfuric acid gave solid barium sulfate and a solution of a contaminated citric acid. In another recovery attempt, treatment of an acidified spent citrate solution with potassium ferrocyanide left substantial quantities of iron in the electrolyte.

A ferrous sulfide precipitation has also been attempted. In this process the iron of the acid complex was precipitated from the spent liquor, as ferrous sulfide by the addition of ammonium sulfide. The reclaimed solution, however, was highly contaminated with free sulfur, sulfide ions and the like and proved unsuitable for reuse in the electrolytic descaling process. In another process benzene-phosphinic acid was added to a spent ammonium citrate solution. Here, however, the iron benzenephosphinate precipitate proved sufficiently soluble in the solution con-



taining the citrate ion to discourage the addition of the benzenephosphinic acid.

An additional process contemplated was the treatment of a spent ammonium citrate solution with ammonia gas under pressure to precipitate out the iron hydroxide. Extreme reaction conditions, however, made this process impractical.

A principal object of the present invention is to provide a novel, simple and inexpensive process for the reclamation of spent electrolyte resulting from the electrolytic descaling of metals as described in said copending application.

Another object of the present invention is to obtain electrolyte in a substantially pure state and high yield for reuse in the electrolytic descaling process of said copending application.

A further object of the present invention is to provide a method for the reclamation of such spent electrolyte thereby eliminating any need for making up fresh electrolyte for use in the electrolytic descaling process of the copending application.

A further object of the present invention is to eliminate the disposal problem of waste acid solutions normally encountered in present descaling processes.

Other and additional objects of this invention will be apparent to those skilled in the art from the ensuing description, examples and drawing.

It has unexpectedly been found that the foregoing objectives can be achieved through the combination of several specific steps. Broadly stated, the reclamation process of this invention comprises contacting the spent solutions of the copending application, particularly the spent solutions therein obtained when using an aqueous salt solution of a chelating acid and an ammonium, potassium or sodium hydroxide as the electrolyte, with a water soluble metal hydroxide, for example, a solid alkali metal hydroxide or an aqueous alkali metal hydroxide solution in order to raise the pH of the spent solution to about 10.5. If desired, prior to treatment with the water soluble metal hydroxide the spent solution can be filtered to remove any insoluble scale or other suspended foreign matter.

The treatment with the water soluble metal base results in the precipitation of the metal which has combined with the acid component of the electrolyte. A substantial portion of said precipitate generally comprises ferric and/or ferrous hydroxide especially when a steel strip is descaled. For effective precipitation of said metal it is essential that the pH of the spent solution be at least 10.5.

The precipitated solids are thereafter separated from the mother liquor by any suitable means, as for example, by filtration, decantation and the like, washed and the washings combined with the mother liquor. It is advantageous prior to the separation of the precipitated solids to heat the mother liquor, on the one hand, to completely drive off from the mother liquor any volatile salt forming ingredients as ammonia released under the basic conditions and which would occur when reclaiming a spent electrolyte derived from an ammonium salt, and, on the other hand, to coagulate the precipitate and to insure the complete precipitation of said metal.

After separation of the precipitated solids, the pH of the mother liquor is adjusted to any desired pH by treatment of the mother liquor with a cation exchange resin, as for example, by passing the mother liquor through one or more cation exchange resin columns. There is thus obtained fresh electrolyte in a substantially pure state which can be returned to the descaling tank for use as the electrolyte in the electrolytic descaling process of said copending application.

If desired, subsequent to the treatment with the cation exchange resin, the concentration and pH of the electrolyte can be adjusted by evaporation, addition of water, and/or base, and/or acid. In regenerating salts of nitrogen bases in particular any ammonium salts it is necessary to add to the reclaimed electrolyte subsequent to its treat-

ment with the cation exchange resin ammonium hydroxide to furnish the ammonium ion and to achieve the desired pH since any ammonium ion originally present in the spent descaling solution is driven off as ammonia in the heat treatment following the treatment with the water soluble metal hydroxide.

Examples of water soluble metal hydroxides employed in the precipitation step are sodium hydroxide and potassium hydroxide. With regeneration of a sodium or potassium citrate solution, the corresponding alkali metal hydroxide is employed in the precipitation step. Sodium hydroxide is normally used in the regeneration of the ammonium citrate solution.

The cation exchange resins play a dominant role in the reclamation process since by means of said cation exchange resins cations in the mother liquor are exchanged for hydrogen ions, the resultant pH of the mother liquor after treatment with the cation exchange resin being dependent on an appropriate selection of the cation exchange resin.

In regeneration of any salt of a nitrogen base, especially a salt of ammonium hydroxide, conventional strong cation exchange resins of the sulfonic acid type, as for example, Amberlite IR-120 are appropriate. Weak and moderately weak cation exchange resins as for example, the conventional weak, cation exchange resins of the carboxylic acid type which have a pKa value of about 6, e.g. Amberlite IRC-50 (a cross-linked polymethacrylic acid type structure) and the moderately weak cation exchange resins of the carboxylic acid type which have a pKa value of about 5 e.g. XE-232 resin (a cross-linked polyacrylic acid structure) can be used but they must be used in combination with a strong cation exchange resin since the use of the weak or moderately weak cation resins reduces the pH to only a slightly acidic value and not to the pH of about 1 to 2 which is required for conversion of the acid component to the free acid which is necessary for the complete removal of alkali ions or other cations. Addition of the nitrogen base as ammonium hydroxide thereupon provides the ammonium ion and the desired pH thus yielding the reusable electrolyte.

In the case of reclaiming aqueous solutions of the salt of an alkali metal hydroxide, exemplary ion exchange resins are: a strong cation exchange resin of the sulfonic acid type or a combination of a moderately weak or weak cation exchange resin with pKa equal to about 6 or 5, respectively, and a strong cation exchange resin; with both types the ion exchange is halted when the pH has been reduced to the value desired for use in the descaling operation, i.e. within the pH range of about 3 to 6.

The cation exchange resins used in the process can be regenerated, i.e., returned to the desired acid state by treatment with dilute acid solutions, e.g., dilute sulfuric acid solutions. Strong cation exchange resins normally require greater than stoichiometric quantities of acid for regeneration. The weak or moderately weak cation exchange resins require an almost stoichiometric acid regeneration. In those cases where a strong cation exchange resin is employed in conjunction with a weak or moderately weak cation exchange resin, if the strong cation exchange resin is regenerated first, the effluent, which now contains the neutral salt and the excess acid, can be used to partially regenerate the weak or moderately weak cation exchange resin. Since the regeneration of the weak or moderately weak resins is nearly stoichiometric, the waste effluent will then be an essentially neutral salt solution, e.g., a sodium sulfate solution if sulfuric acid were used to regenerate the resins. Thus free acid in the waste stream can be eliminated.

Referring to the flow chart forming the drawing accompanying the present application and illustrating with a spent citrate solution from an electrolytic descaling bath utilizing as the electrolyte an ammonium citrate solution with a pH of about 5, the spent solution is withdrawn from the electrolytic descaling tank (Zone 1) to



a storage reservoir (Zone 2). Any insoluble or other suspended foreign matter is then removed by filtration and the filtrate treated with sufficient sodium hydroxide to raise the pH of the solution to at least about 10.5 to cause substantially complete precipitation of the chelated or complexed metal. The solution and precipitate (Zone 3) are then heated to insure complete precipitation. A desirable temperature value is generally around 100° F. although such may be lowered or raised depending upon the speed of precipitation desired. The precipitate is next separated from the mother liquor by filtering and if desired the complexing metal recovered from the precipitate by subsequent treatment. The filtrate (Zone 4) consists of a highly basic aqueous solution containing sodium ions and citrate ions.

To effect conversion of the filtrate (Zone 4) to a solution of ammonium citrate having a pH of within the range of about 3 to 7, the filtrate is passed through an appropriate cation exchange resin column wherein the sodium ions of the filtrate are exchanged for hydrogen ions thus yielding a citric acid solution (Zone 5), the pH of the resultant solution being about 1 to 2. The concentration and pH of the citric acid solution (Zone 5) is then adjusted to the desired value by the evaporation of water or addition of water and/or citric acid together with the addition of ammonium hydroxide. The reclaimed ammonium citrate solution (Zone 6) is then returned to the electrolytic descaling tank (Zone 1) for reuse in the electrolytic descaling process.

The invention will be better understood by reference to the following examples. These exemplary embodiments are intended to be merely illustrative and not restrictive of the invention, the scope of which is defined in the appended claims. It is to be understood that the invention is susceptible of embodiment in various forms all falling within the scope of the claims which follow and which are apparent to those skilled in the art from the present specification.

#### Example 1

Fifty milliliters of a spent electrolyte solution resulting from the electrolyte descaling of steel strip with an ammonium citrate solution of pH of about 5 and a concentration of citric acid of about 28 percent by weight per liter of solution, were diluted with 50 milliliters of water. Fifteen milliliters of a five percent by weight of aqueous sodium hydroxide were added to obtain a minimum pH of about 10.5 and to precipitate the chelated metal, and the solution then heated to drive off the ammonia. The solids were filtered off and washed. The resulting strongly basic solution was treated with a strong cationic exchange resin (Amberlite IR-120) until the pH of the solution was about 1 to 2. The concentration and pH of the solution was thereupon adjusted to the desired values by addition of ammonium hydroxide and water. The solution was now ready for use as the electrolyte in the electrolytic descaling process described in said copending application.

#### Example 2

Spent citrate solution resulting from the electrolytic descaling of strip steel employing as the electrolyte a sodium citrate solution having a pH of about 4.6 and a concentration of citrate component of about 28 percent by weight per liter of solution was treated with sufficient sodium hydroxide to raise the pH of the solution to at least about 10.5. The precipitated solids were removed and the filtrate, diluted with water, and having a pH of about 10.5 was passed down a 2-inch plexiglass column containing a weak cation resin having a pKa value of 6.0 (Amberlite IRC-50). The effluent having a pH of 5.5 was subsequently treated with a strong cationic exchange resin (Amberlite IR-120) and thereupon concentrated by evaporation to the original volume of the spent citrate solution to produce a sodium citrate solution with a pH of 4.6 suitable for use as the electrolyte in the electrolytic descaling process as described in said copending application.

While there have been described herein certain embodiments of the invention, it will be obvious to those skilled in the art that modifications and changes may be made therein without departing from the essence of the invention. It is, therefore, to be understood that the exemplary embodiments and drawings are illustrative and not restrictive of the invention, the scope of which is defined in the following claims, and that all modifications that come within the meaning and range of equivalency of the claims and would be obvious to those skilled in the art, are intended to be included therein.

Also the terms and expressions which have been employed in the specification are used as terms of description and not of limitation, and there is no intention, in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, since it is recognized that various modifications are possible within the scope of the invention claimed.

Having described the present invention in some detail, that which is sought to be protected is set forth in the following claims.

What is claimed is:

1. Process for producing a reusable, substantially pure electrolyte for electrolytic descaling by reclaiming a spent aqueous electrolyte resulting from the electrolytic descaling of steel with an aqueous solution consisting essentially of a salt of gluconic acid, tartaric acid, diglycolic acid, glycolic acid or citric acid, said salt solution having a pH of about 3 to 7, which comprises contacting the spent aqueous electrolyte with a water soluble hydroxide sufficient to raise the pH of the spent aqueous electrolyte to at least about 10.5, separating the precipitated solids and contacting the resultant solution with at least one cation exchange resin such that the pH of the solution is reduced to at least 7.

2. Process according to claim 1 in which any insoluble material is removed from the spent aqueous electrolyte solution prior to treatment of the solution with said water soluble hydroxide.

3. Process for producing a reusable, substantially pure electrolyte for electrolytic descaling by reclaiming a spent aqueous electrolytic solution resulting from the electrolytic descaling of steel with an aqueous solution consisting essentially of a salt of gluconic acid, tartaric acid, diglycolic acid, glycolic acid or citric acid, and a nitrogen base, said salt solution having a pH of about 3 to 7, which comprises contacting the spent aqueous electrolytic solution with a water soluble hydroxide sufficient to raise the pH of the spent aqueous electrolyte to at least about 10.5 heating the resultant suspension to drive off any volatile salt forming ingredients, separating the precipitated solids, treating the resultant solution with at least one cation exchange resin in such a manner that the pH of the solution is reduced to about 1 to 2 and the acid component is converted to the free acid and thereupon raising the pH of the solution to about 3 to 7 with a nitrogen base.

4. Process for producing a reusable, substantially pure electrolyte for electrolytic descaling by reclaiming a spent aqueous electrolytic solution resulting from the electrolytic descaling of steel with an aqueous solution consisting essentially of a salt of gluconic acid, tartaric acid, diglycolic acid, glycolic acid or citric acid, and ammonium hydroxide, said salt solution having a pH of about 3 to 7, which comprises contacting the spent aqueous electrolytic solution with a water soluble hydroxide sufficient to raise the pH of the spent aqueous electrolyte to at least about 10.5, heating the resultant suspension to drive off any volatile salt forming ingredients, separating the precipitated solids, treating the resultant solution with at least one cation exchange resin in such a manner that the pH of the solution is reduced to about 1 to 2 and the acid component is converted to the free acid, and thereupon raising the pH of the solution to about 3 to 7 with ammonium hydroxide.

5. Process for producing a reusable, substantially pure



electrolyte for electrolytic descaling by reclaiming a spent aqueous electrolytic solution resulting from the electrolytic descaling of steel strip with an aqueous solution consisting essentially of ammonium citrate having a pH of about 5, which comprises contacting the spent aqueous electrolytic solution with aqueous sodium hydroxide to raise the pH of the spent aqueous electrolyte to at least about 10.5, heating the resultant suspension to drive off any volatile salt forming ingredients, separating the precipitated solids, treating the resultant solution with at least one strong cation exchange resin such that the pH of the solution is reduced to about 1 to 2 and the acid component is converted to the free acid, and thereupon adjusting the pH of the solution to about 5 by the addition of ammonium hydroxide.

6. Process for producing a reusable substantially pure electrolyte for electrolytic descaling by reclaiming a spent aqueous electrolytic solution resulting from the electrolytic descaling of strip steel with an aqueous solution consisting essentially of sodium citrate, having a pH of about 4.6, which comprises contacting the spent aqueous electrolyte with sodium hydroxide sufficient to raise the pH of the spent aqueous electrolyte to at least about 10.5, separating the precipitated solids, and reducing the pH of the resultant solution to a pH of about 4.6 by treatment with at least one cation exchange resin.

7. Process for producing a reusable, substantially pure electrolyte for electrolytic descaling by reclaiming a spent aqueous electrolytic solution resulting from the electrolytic descaling of steel with an aqueous solution consisting essentially of a salt of gluconic acid, tartaric acid, diglycolic acid, glycolic acid or citric acid, and an alkali metal hydroxide, said salt solution having a pH of about 3 to 6, which comprises contacting the spent aqueous electrolyte with an alkali metal hydroxide sufficient to raise the pH of the spent aqueous electrolyte to at least about 10.5, separating the precipitated solids, contacting the resultant filtrate with at least one cation exchange resin such that the pH of the filtrate is reduced to a value of about 3 to 6.

8. Process according to claim 7 in which any insoluble material is removed from the spent aqueous electrolyte solution prior to treatment of the solution with said alkali metal hydroxide.

9. Process for producing a reusable, substantially pure electrolyte for electrolytic descaling, by reclaiming a spent aqueous electrolytic solution resulting from the electrolytic descaling of steel with an aqueous solution consisting essentially of potassium citrate having a pH of about 3 to 6, which comprises contacting the spent aqueous electrolyte with potassium hydroxide sufficient to raise the pH of the spent aqueous electrolyte to at least about 10.5,

separating the precipitated solids, and reducing the pH of the resultant solution to a pH of about 3 to 6 by treatment with at least one cation exchange resin.

10. Process for producing a reusable, substantially pure electrolyte for electrolytically descaling by reclaiming a spent aqueous electrolytic solution resulting from the electrolytic descaling of strip steel with an aqueous solution consisting essentially of sodium citrate, having a pH of about 4.6, which comprises contacting the spent aqueous electrolyte with sodium hydroxide sufficient to raise the pH of the spent aqueous electrolyte to at least about 10.5, coagulating the precipitated solids, separating the precipitated solids, and reducing the pH of the resultant solution to a pH of about 4.6 by treatment with at least one cation exchange resin.

11. Process for producing a reusable, substantially pure electrolyte for electrolytic descaling by reclaiming a spent aqueous electrolytic solution resulting from the electrolytic descaling of steel with an aqueous solution consisting essentially of a salt of gluconic acid, tartaric acid, diglycolic acid, glycolic acid or citric acid, and an alkali metal hydroxide, said salt solution having a pH of about 3 to 6, which comprises contacting the spent aqueous electrolyte with an alkali metal hydroxide sufficient to raise the pH of the spent aqueous electrolyte to at least about 10.5, coagulating the precipitated solids, separating the precipitated solids, contacting the resultant filtrate with at least one cation exchange resin such that the pH of the filtrate is reduced to a value of about 3 to 6.

12. Process for producing a reusable, substantially pure electrolyte for electrolytic descaling, by reclaiming a spent aqueous electrolytic solution resulting from the electrolytic descaling of steel with an aqueous solution consisting essentially of potassium citrate, which comprises contacting the spent aqueous electrolyte with potassium hydroxide sufficient to raise the pH of the spent aqueous electrolyte to at least about 10.5, coagulating the precipitated solids, separating the precipitated solids, and reducing the pH of the resultant solution to a pH of about 3 to 6 by treatment with at least one cation exchange resin.

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