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Smith

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[54] **REGENERATING ANION EXCHANGE ZONE CONTAINING HEXAVALENT CHROMIUM**

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[52] **U.S. Cl.** ..... **423/54;** 423/658.5; 210/30; 210/31; 210/32; 210/37; 210/38; 204/51; 75/101 BE

[51] **Int. Cl.**..... **C01g 37/14;** B01d 15/06

[58] **Field of Search** ..... 423/54, 658.5; 204/51; 210/37, 38, 30–32; 75/101 BE

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Primary Examiner—Herbert T. Carter

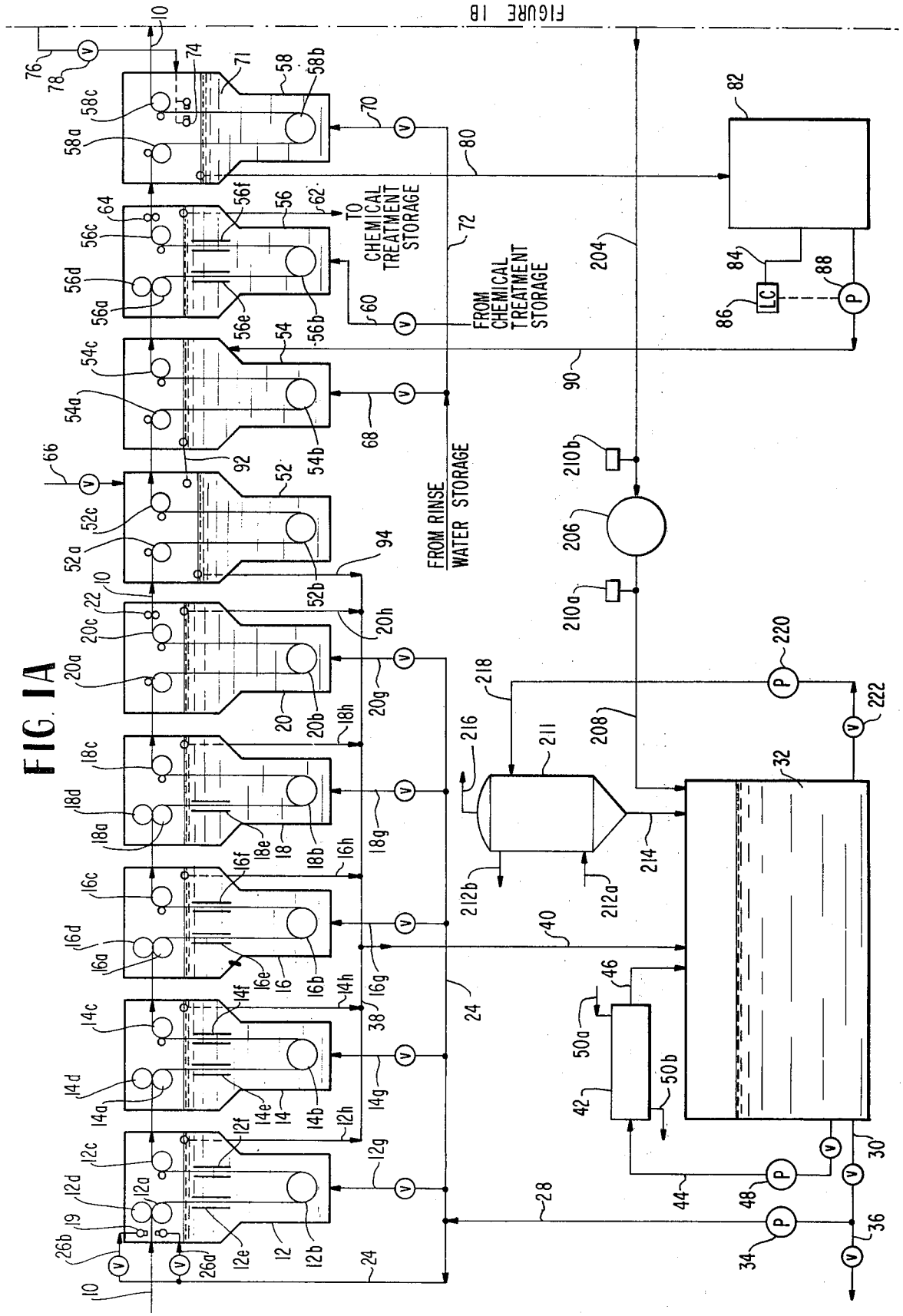
Attorney, Agent, or Firm—Shanley, O'Neil and Baker

[57] **ABSTRACT**

In recovering hexavalent chromium from chrome plated steel strip which is wetted with plating solution as a result of dragout from the plating process, an aqueous solution containing hexavalent chromium in relatively low concentration is concentrated in a process comprising treating in a first cation exchange zone, treating in an anion exchange zone, regenerating the anion exchange zone and treating the effluent of regeneration in a cation exchange zone different from the first cation exchange zone. The concentrated solution is passed to a storage zone and recirculation is carried out between the storage zone and the plating zone and solution is passed from the storage zone to an evaporation zone and more concentrated solution is passed from the evaporation zone to the storage zone. In regenerating the anion exchange zone, only a portion of the hexavalent chromium is removed.

8 Claims, 2 Drawing Figures

FIG. IA


FIGURE 1B
TO CHEMICAL TREATMENT STORAGE
FROM CHEMICAL TREATMENT STORAGE
FROM RINSE WATER STORAGE
LC

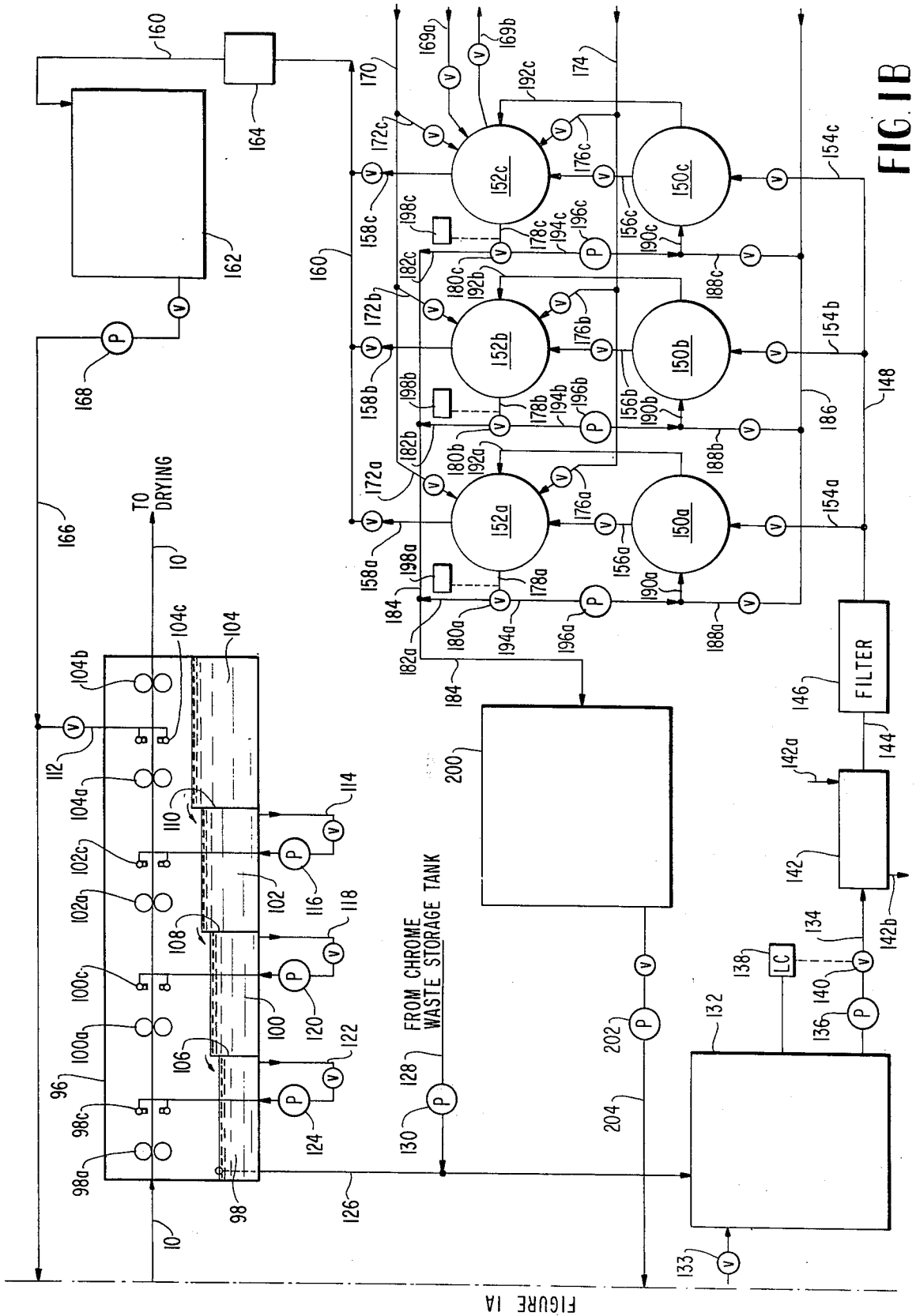

TO DRYING
FROM CHROME WASTE STORAGE TANK
FILTER
LC
FIGURE 1A

FIG. 1B

REGENERATING ANION EXCHANGE ZONE CONTAINING HEXAVALENT CHROMIUM

BACKGROUND OF THE INVENTION

This invention relates to regenerating an anion exchange zone incident to recovering hexavalent chromium and increasing the concentration of the same in aqueous solution. Such allows practical use for plating of chromium values which would otherwise be lost.

Methods have been disclosed for recovery of hexavalent chromium involving washing plated articles wetted with chromium-containing solution, recovering an aqueous solution containing hexavalent chromium in relatively high concentration, recovering an aqueous solution containing hexavalent chromium in relatively low concentration, concentrating low concentration solution by ion exhange and regeneration of an anion exchanger, and concentrating by evaporation. In this regard, see Paulson et al, *Plating*, pages 1000–1009, September, 1953; Culotta et al, *Plating*, pages 251–255, March, 1970; Zievers et al, U.S. Pat. No. 3,658,470.

It is an object of this invention to provide a novel method of regenerating an anion exchange zone in which resin in the hydroxide form has been used to remove hexavalent chromium in the form of anions from a solution, whereby to maximize the concentration of hexavalent chromium in the effluent provided by regeneration.

This object and others will be evident from the following detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1A and 1B constitute a flowsheet depicting a process for chrome plating steel strip and for recovering hexavalent chromium from the solution wetting the plated strip for reuse and illustrate the inventive concepts herein.

DETAILED DESCRIPTION

With continuing reference to FIGS. 1A and 1B of the drawings, steel strip having been preliminarily treated, for example in electrolytic cleaning and pickling steps, follows a travel path **10** and passes successively through chrome plating tanks **12, 14, 16** and **18** which define a plating zone. In each of the plating tanks **12, 14** and **16,** the strip follows the travel path so as to enter a plating tank in a substantially horizontal plane, then passes over a contact roll and advances downwardly, then passes under a sink roll and advances upwardly, then passes over another contact roll and leaves the tank in a substantially horizontal plane. In the plating tank **18,** the strip follows the travel path so as to enter the tank in a substantially horizontal plane, then passes over a contact roll and advances downwardly, then passes under a sink roll and advances upwardly, then passes over a deflector roll and leaves the tank in a substantially horizontal plane. In FIG. 1A the contact rolls at the strip entrance sides of tanks **12, 14, 16** and **18** are respectively denoted **12***a*, **14***a*, **16***a*, and **18***a;* the sink rolls are respectively denoted **12***b*, **14***b*, **16***b*, and **18***b;* the contact rolls at the exit sides of the tanks **12, 14** and **16** are respectively denoted **12***c*, **14***c*, and **16***c;* and the deflector roll at the exit side of tank **18** is denoted **18***c*. The contact rolls **12***a*, **14***a*, **16***a*, **18***a*, **12***c*, **14***c*, and **16***c* perform a deflecting function and also render the strip cathodic. At the entrance end of each of the tanks **12,** 14, 16 and **18,** snubber rolls respectively denoted **12***d*, **14***d*, **16***d* and **18***d* force the strip against adjacent contact rolls to provide good contact.

In the first three tanks, that is tanks **12, 14** and **16,** there are two sets of anodic grids which are vertically oriented with one of the sets being between the contact roll at the entrance end of a tank and a sink roll and the other set being between a sink roll and the contact roll at the exit end of a tank so that the strip passes through one set of grids on its downpass through a tank and through the other set on its up pass. The grids for the downpass are respectively denoted **12***e*, **14***e* and **16***e*, and the grids for the up pass are respectively denoted **12***f*, **14***f* and **16***f*. In the fourth tank, tank **18,** there is only one set of vertically oriented grids, and this set is between the contact roll at the strip entrance end of the tank and the sink roll **50** that the strip passes through this set on the downpass and does not pass between any grids on the up pass; this set of grids is denoted **18***e*.

The electrolyte in each of the tanks **12, 14, 16** and **18** is the same, namely an aqueous solution of chromic acid, and is depicted as a body of liquid in each tank extending to a level above the anodic grids. The chemistry of chromic acid is quite complicated and what exactly is present is not known. However, at the pH of less than 1 which is characteristic of the electrolyte utilized, the chromic acid is mostly in the form of dichromic acid ($H_2Cr_2O_7$). The concentration in the electrolyte of the chromic acid expressed as grams of CrO_3 per liter is in the range of 140 to 250. Small amounts of silicofluorides (magnesium, sodium or potassium) and sulfate in the form of sulfuric acid are typical additives.

Prewet sprays **19** are present at the entrance end of tank **12** upstream of contact roll **12***a* to spray plater solution, that is electrolyte, at each side of strip before it reaches the contact roll. The reason for this is to put a good conducting medium on the strip so that it will make good contact with the contact roll thereby negating arcing between the contact roll and the strip.

The strip having been chrome plated exits from tank **18** and follows travel path **10** through a tank **20.** The strip enters the tank **20** in a horizontal plane, passes over a deflector roll **20***a*, then turns downwardly traveling vertically, then passes under a sink roll **20***b*, then advances vertically upwardly and passes over a deflector roll **20***c* and then advances horizontally out of the tank. The tank **20** contains the same solution as each of the plating tanks **12, 14, 16** and **18** but no electrolytic action is imparted during the passage of the strip through this solution. Passage of the strip through the tank **20** has the effect of removing objectionable oxide coating from the strip.

At the exit side of tank **20** downstream of deflector roll **20***c* is a pair of wringer rolls **22** between which the strip passes. These rolls **22** wipe plater solution from the strip to minimize dragout of electrolyte from the plating process.

The tanks **12, 14, 16, 18** and **20** are continuously supplied with electrolyte, that is plater solution, respectively through valved lines **12***g*, **14***g*, **16***g*, **18***g* and **20***g*. These lines are supplied with plating solution by a header **24.** Header **24** also communicates with valved lines **26***a* and **26***b* which in turn communicate with sprays **19.** The header **24** communicates with and is fed by line **28** which in turn communicates with and is fed by valved line **30** which in turn communicates with plater solution storage tank **32** which defines a plater solu-

tion storage zone. A pump **34** is provided in line **28** to continuously move the plater solution from tank **32** via lines **30** and **28** and into header **24** and from there via lines **26***a* and **26***b* and **12***g*, **14***g*, **16***g*, **18***g* and **20***g* into tanks **12, 14, 16, 18** and **20.** A valved line **36** communicates with line **30** so that plater solution can be drained from the system. Overflow outlets are provided in each of the tanks **12, 14, 16, 18** and **20,** and plater solution continuously overflows through these outlets through the respective lines **12***h*, **14***h*, **16***h*, **18***h* and **20***h*. These overflow lines communicate at their downstream ends into a main exit line **38** which communicates with another line **40** which in turn communicates with the plater storage tank **32.** Thus, there is provided between tank **32** and between tanks **12, 14, 16, 18** and **20** a recirculation loop whereby recirculation is continuously carried out between the storage zone defined by tank **32** and the plating zone defined by tanks **12, 14, 16** and **18.**

The plater storage tank **32** is also in a recirculation loop with a heat exchanger **42** defining a heat exchange zone with a valved line **44** communicating between tank **32** and heat exchanger **42** and line **46** leading back from heat exchanger **42** into storage tank **32.** Line **44** contains a pump **48** whereby plater solution is recirculated through this loop. Water is passed through heat exchanger **42** countercurrent to the plater solution as indicated by lines **50***a* and **50***b* to remove heat from the plater solution (that is, from the plating solution storage zone defined by tank **32**). This is done because there is a heat buildup in the plating portion of the system due to the grid current. In other words, the heat gained because of the current supplied by the grids exceeds the heat lost through the tanks and pipes of the system. Inasmuch as the best cathode efficiency is achieved utilizing a plater solution having a temperature of 105° to 125°F., control of heat buildup is desirable.

The chrome plated strip having had undesirable oxides removed in tank **20** and having passed through wringer rolls **22** still is wetted with a significant amount of plating solution comprising aqueous chromic acid solution. So as to recover the hexavalent chromium from such solution, the strip is advanced along travel path **10** through a first rinse tank **52** and a second rinse tank **54.** The strip is then passed through a chemical treatment tank **56.** The strip is then passed through a third rinse tank **58** to recover hexavalent chromium from solution wetting the strip.

The tank **52** contains a strip entrance end deflector roll **52***a*, a sink roll **52***b* and a strip exit end deflector roll **52***c* and the strip following travel path **10** turns downwardly over roll **52***a* and moves vertically downwardly turning under roll **52***b* and then advances vertically upwardly over roll **52***c* whereupon it leaves tank **52.**

The tank **54** contains a strip entrance end deflector roll **54***a*, a sink roll **54***b* and a strip exit end deflector roll **54***c*. The strip entering tank **54** after passage out of tank **52** turns downwardly over roll **54***a* and moves vertically downwardly, then turns under roll **54***b*, and then advances vertically upwardly and turns over roll **54***c* and moves out of tank **54.**

The tank **56** contains a strip entrance end contact roll **56***a*, a sink roll **56***b* and a strip exit end contact roll **56***c*. The strip exiting from tank **54** passes over roll **56***a* and then passes vertically downwardly, then passes under roll **56***b*, then advances vertically upwardly and passes over roll **56***c* exiting from tank **56** horizontally.

The tank **58** contains a strip entrance end deflector roll **58***a*, a sink roll **58***b* and a strip exit end deflector roll **58***c*. The strip exiting from tank **56** passes into tank **58** and over roll **58***a*, then advances vertically downwardly, then passes under roll **58***b*, then passes vertically upwardly, then passes over roll **58***c* and exits horizontally from tank **58.**

In tanks **52** and **54,** the strip is subjected to rinsing to wash off plater solution on the strip by dragout from the plater tanks **12, 14, 16** and **18** and from tank **20.** In the chemical treatment tank **56,** the strip is subjected to electrolytic treatment to provide a hexavalent chrome oxide coating. In tank **58,** washing is provided to remove solution on the strip by dragout from the chem treat tank **56.**

In the chemical treatment tank, the electrolyte is preferably aqueous chromic acid solution containing **35** grams per liter of chromic acid expressed as CrO_3. Electrolytic action is supplied in this tank, and it operates and is constructed generally as one of the plater tanks **12, 14, 16** or **18** with vertically oriented anodic grids **56***e* and **56***f* on either side of the strip respectively on a downpass and on an up pass and contact rolls **56***a* and **56***c* rendering the strip cathodic and snubber roll **56***d* forcing the strip against contact roll **56***a* at the inlet to the tank. As with the plater tanks, a dc current is supplied. The electrolyte is initially supplied into the tank **56** from a chemical treatment storage tank, not depicted, via valved line **60.** Solution is recirculated between the chemical treatment tank and the chemical treatment storage tank during the progress of the process with electrolyte flowing from the storage tank into tank **56** via line **60** and returning to the chemical treatment tank by overflow gravity feed via line **62.** The recirculation loop includes a heat exchanger, not depicted, where recirculating solution passes in indirect heat exchange with hot water to heat the recirculating liquid and control the temperature of solution in the storage tank, for example to 105°. A pair of wringer rolls **64** on either side of the strip at the exit end of tank **56** wipe electrolyte from the strip and minimize the amount of the electrolyte leaving the tank **56** by dragout on the strip.

The tanks **52, 54** and **58** make up an interconnected washing system with washing solution passing counterflow to the strip wherein the strip is washed in a first washing step to recover an aqueous solution comprising a relatively high concentration of hexavalent chromium in the form of anions.

On startup, rinse solution, preferably demineralized water is introduced into tank **52** via valved line **66.** Also, rinse solution is initially introduced into tank **54** through valved line **68** and into tank **58** through a valved line **70.** Lines **68** and **70** are supplied through header **72** which is supplied from a rinse water storage tank, not depicted.

During the process, demineralized water is added continuously into tank **58** through spray nozzles **74** which are supplied by line **76** containing valve **78.** The spray nozzles **74** are on either side of the strip in tank **58** on its up pass just prior to its passage over roll **58***c*. Flow through the spray nozzles **74** is perferably controlled to maintain a CrO_3 concentration in tank **54** equal to the CrO_3 concentration in tank **56** by manually setting the flow through the nozzles and controlling

valve 78 in response to periodic chemical tests carried out on tank 54 solution. These sprays aid in washing off residual electrolyte, that is aqueous hexavalent chromium containing solution, on the strip by dragout from tank 56. Washing action is also provided by a bath 71 in the bottom of tank 58 through which the strip passes in its downpass and in its up pass through tank 58. The demineralized water introduced through the sprays 74 and solution washed off of the strip by these sprays falls by gravity into the lower portion of tank 58 and becomes part of the bath 71. Solution continuously overflows through an overflow outlet in tank 58 providing a constant level in that tank.

The liquid leaving tank 58 through its overflow outlet enters a line 80 and flows therethrough by gravity into a collection tank 82. The level of liquid in tank 82 is sensed by lever sensor 84. A level controller 86 operates in response to the level sensed, and a pump 88 operating in response to a set point on the controller 86 operates to pump solution from tank 82 via a line 90 into tank 54.

The tank 54 has an overflow outlet, and this acting in concert with addition of solution through line 90 provides a substantially constant level bath in tank 54. The strip passing through tank 54 is washed by the bath on its downpass and up pass through tank 54 whereby aqueous hexavalent chromium containing solution on the strip by dragout from the plating tanks and tank 20 is rinsed therefrom.

Solution passes out of the overflow outlet in tank 54 and passes via a line 92 into tank 52. A substantially constant level of rinse solution is maintained in the lower portion of tank 52 as a result of an overflow outlet in that tank. The bath of rinse solution in tank 52 provides washing of the strip on its downpass from roll 52*a* to roll 52*b* and on its up pass from roll 52*b* to roll 52*c* whereby aqueous hexavalent chromium containing solution on the strip by dragout from the plating tanks and tank 20 is washed therefrom.

Solution overflows through the outlet in tank 52, flows by gravity through a line 94 and then into main line 38 and through line 40 into plater storage tank 32.

The concentration of chromic acid expressed as CrO_3 in the baths in each of the tanks 52, 54 and 58 is as follows: in the bath in tank 52, 85 to 100 grams per liter; in the bath in tank 54, 30 to 40 grams per liter, perferably 35; in the bath 71 in tank 58, 5 to 15 gram per liter, preferably 10. These concentrations are controlled by control of valve 78.

Following its exit from tank 58, the chrome plated strip still wetted with some aqueous hexavalent chromium containing solution, for example one-tenth of the amount removed in the prior washing in tanks 52, 54 and 58 continues along travel path 10 through a spray washer 96 depicted in FIG. 1B wherein the strip is washed in a second washing step to recover an aqueous solution comprising cations (for example, iron and trivalent chromium ions) and a relatively low concentration of hexavalent chromium in the form of anions.

The spray washer comprises four open top compartments 98, 100, 102 and 104 in series along its length with compartment 98 at its strip entrance end, followed by compartment 100, followed by compartment 102 and finally followed by compartment 104 at its strip exit end. A wall 106 separates compartments 98 and 100. A wall 108 separates compartments 102 and 100. A wall 110 separates compartments 104 and 102. The wall 110 has a greater vertical dimension than the wall 108 and the wall 108 has a greater vertical dimension than the wall 106. The strip advancing in its travel path 10 through the spray washer 96 passes first over compartment 98, then over compartment 100, then over compartment 102 and then over compartment 104. The strip path over the compartments is a straight line path and is horizontally oriented. There are five sets of wringer rolls that guide the strip over the compartments in the horizontal path. These sets of wringer rolls are respectively denoted 98*a*, 100*a*, 102*a*, 104*a* and 104*b* with set 98*a* being at the strip entrance end of the washer over compartment 98, set 100*a* being over compartment 100 near wall 106, set 102*a* being over compartment 102 near wall 108, set 104*a* being over compartment 104 near wall 110 and 104*b* being near the strip exit end of the washer 96.

Over each of the compartments 98, 100, 102, 104 there are two spray nozzles, one below the strip and one above the strip so that the strip is sprayed from above and below. The spray nozzles above tank 98 are denoted 98*c*; those above compartment 100 are denoted 100*c*; those above compartment 102 are denoted 102*c* and those above compartment 104 are denoted 104*c*. Spray nozzles 104*c* are supplied with demineralized water by valved line 112. The water from the spray nozzles 104*c* washes residual solution containing hexavalent chromium from the strip, and the resultant solution falls by gravity into compartment 104 where it builds up to the level of the top of wall 110 and then continuously cascades from compartment 104 into compartment 102. Solution is pumped from the bottom of compartment 102 through a valved line 114 by a pump 116 to the spray nozzles 102*c*. The solution from the nozzles 102 washes residual solution containing hexavalent chromium from the strip and resultant solution falls into compartment 102. The solution in compartment 102 accumulates to the level of the top of wall 108 and then continuously cascades over this wall into compartment 100. Solution from the bottom of compartment 100 flows through a valved line 118 and is pumped by a pump 120 to spray nozzles 100*c*. Solution from the spray nozzles 100*c* washes residual solution containing hexavalent chromium from the strip and the resultant solution falls into compartment 100. Solution accumulates in compartment 100 to fill that compartment and thereafter cascades over wall 106 into compartment 98. Solution flows from the bottom of compartment 98 through a valved line 122 and is pumped by a pump 124 to spray nozzles 98*c*. Solution from the spray nozzles 98*c* washes residual solution containing hexavalent chromium from the strip and the resultant liquid falls into compartment 98. Solution overflows from compartment 98 into line 126.

The spray washer 96 constitutes a counterflow spray washing system whereby solution on the strip containing hexavalent chromium is washed therefrom and a solution comprising cations (for example, iron and trivalent chromium ions) and a relatively low concentration of hexavalent chromium, that is, for example, from 0.1 to 0.3 grams per liter of chromic acid expressed as CrO_3, overflows into line 126. When the strip leaves washer 96, it contains only trace or no amounts of chromic acid wetting it.

The strip exiting from the spray washer is dried and coiled.

Merging with line **126** is a line **128** containing a metering pump **130.** The upstream end of line **128** communicates with a chrome waste storage tank, not shown in the drawings. Various of the tanks can be emptied into the chrome waste storage tank, for example on shut down, to capture chrome laden water which can be metered by pump **130** into line **126** for chrome recovery.

Solution from line **126** enters a collection tank **132** having an exit line **134.**

Valved line **133** is provided communicating with tank **132** for the passage thereto of chrome laden water from sources other than compartment **98** and line **128**; for example, chrome laden water from washing strip exiting from a chemical treatment step in an electrotinplating line can be passed into tank **132** through line **133.**

The valved lines **128** and **133** constitute means for admixing aqueous solution recovered from the second washing step with hexavalent chromium containing solution from other sources to provide in tank **132** an admixture which is an aqueous solution comprising cations and a relatively low concentration of hexavalent chromium in the form of anions.

Solution is pumped from tank **132** by a pump **136** in line **134** in response to a level control **138** operating a valve **140** in line **134.** The pump **136** runs continuously and the level control operates to close the valve more if the level in the tank drops. This setup operates to provide continuous flow through line **134.**

The solution from line **134** flows through heat exchanger **142** where it is cooled against the countercurrent flow of cold water as denoted by arrows **142***a* and **142***b*. Cooling is to a temperature suitable for treatment of the solution in the ion exchange system which is described below.

Solution leaves the heat exchanger **142** via a line **144** and passes through a filter **146** which removes particles of solid material. The filtered solution flows through line **148** into an ion exchange system which is described below.

The ion exchange system comprises three sets of ion exchangers, each set consisting first of a cation exchanger defining a first cation exchange zone and then of an anion exchanger defining an anion exchange zone. The cation exchangers are denoted **150***a*, **150***b* and **150***c*. The anion exchanger associated with cation exchanger **150***a* is denoted **152***a;* the anion exchanger associated with cation exchanger **150***b* is denoted **152***b;* and the anion exchanger associated with cation exchanger **150***c* is denoted **152***c*. Valved lines **154***a*, **154***b* and **154***c* respectively communicate between line **148** and cation exchangers **150***a*, **150***b*, and **150***c*. Line **156***a* communicates between cation exchanger **150***a* and anion exchanger **152***a;* line **156***b* communicates between cation exchanger **150***b* and anion exchanger **152***b;* and line **156***c* communicates between cation exchanger **150***c* and anion exchanger **152***c*. The lines **156***a*, **156***b* and **156***c* each contain valves. Three sets of the ion exchangers are provided so that two sets can be on line while the exchangers of the other set are being regenerated.

Resins for use in the cation exchangers **150***a*, **150***b* and **150***c* are of the strong acid type and are in the hydrogen form. They contain sulfonic acid functional groups and are prepared, for example, by the nuclear sulfonation of styrenedivinylbenzene. These resins are not as highly oxidative resistant as the resins utilized in the cation exchanger for treating regeneration effluent which is described later. Suitable cation exchange resins are, for example, Amberlite IR-120 or Amberlite IR-120 Plus manufactured by Rohm and Haas Company.

The ion exchange resin for use in the anion exchangers is a strong base anion exchange resin of the quaternary ammonium type. It is utilized in the hydroxide form. A suitable resin is Amberlite IRA-900 which is supplied in the chloride form and is converted to the hydroxide form for use; it is available from Rohm and Haas Company.

Solution flows from line **148** into whichever two of the cation exchangers **150***a*, **150***b* and **150***c* are on stream. The cation exchangers take out cations, including trivalent chromium and iron ions and replace them with hydrogen ions. Effluent from a cation exchanger is aqueous solution containing hexavalent chromium in the form of anions, other anions and hydrogen ions and flows into an associated anion exchanger **152***a*, **152***b* or **152***c*. The anion exchangers take out hexavalent chromium in the form of anions and other anions and replace these with hydroxyl ions. Effluent from the anion exchangers is demineralized water. Valved exit lines for flow of effluent from anion exchangers **152***a*, **152***b* and **152***c* are respectively denoted **158***a*, **158***b* and **158***c*.

The lines **158***a*, **158***b* and **158***c* each communicate with a main line **160** whereby demineralized water effluent flows into a demineralized water storage tank **162.** Included in the line **160** is a device **164** for deaerating the demineralized water. The storage tank **162** has a valved exit line **166** for flow of water to lines **112** (see FIG. 1B) and **76** (see FIG. 1A). A pump **168** is provided in line **166** to pump the water through line **166.**

When a set of ion exchange units is to be regenerated, it is isolated from flow from line **148** and from line **160** by closing the appropriate valves, and another set of ion exchange units is brought into communication with line **148** and line **160.**

Regeneration of the cation exchange unit in a set of units is carried out, for example as suggested by the manufacturer of the particular resin utilized, and the particular method of regeneration forms no part of the present invention. Regeneration of a cation exchange unit can be carried out for example, by backwashing, introducting **10%** sulfuric acid as a regenerating agent and rinsing.

Regenerating of an anion exchange unit involves a regeneration cycle comprising backwashing, removal of residual backwash water, introduction of regenerating agent, removal of resulting solution, introduction of rinse water and removal of resulting solution, introduction of water, and recirculation. For simplification purposes some valves associated with these steps are not depicted. For further simplification, the state of each valve in the system at each point in time during the cycle will not be described; the conduits described as functioning at a particular point in time are open or have valves positioned as otherwise described and the other conduits in the regeneration system at that point in time are closed unless otherwise stated. The regeneration is carried out to produce an aqueous effluent comprising cations (from the regenerating agent) and a concentration of hexavalent chromium in the form of anions substantially higher than the relatively low concentration leaving compartment **98** or in tank **132.** Re-

generation of an anion exchange unit is described in detail below.

Backwashing of the anion exchange column is carried out to fluff up the resin and remove extraneous solids and resin fines from the resin bed to permit good contact between the resin and regenerating agent so that regeneration is carried out efficiently. Backwash water having cations removed therefrom, for example by passage through the cation exchanger associated with the anion exchanger being regenerated, is introduced into the bottom of the anion exchange column (the flows other than backwash flows through the various ion exchange columns herein are from the top as is conventional; however, the direction of flow constitutes no part of the present invention). Piping from the introduction of backwash water is represented by valved line **169***a*, and piping for outlet of backwash water is represented by valved line **169***b*, both depicted as associated with column **152***c*. Corresponding piping is provided for columns **152***a* and **152***b* but such is not depicted. When backwashing has been completed, the valve in the appropriate backwash water introduction line (for example **169***a*) is closed. Residual backwash water is removed from the anion exchanger utilizing a pressurized air purge. An air supply line **170** supplies pressurized air for this purpose with communication between line **170** and exchangers **152***a*, **152***b* and **152***c* being provided respectively by valved lines **172***a*, **172***b* and **172***c*. Solution leaves the column during backwashing and the subsequent purging via backwash outlet line (for example, line **169***b*) and is routed to waste disposal.

After backwash water has been so purged, pressurized air flow is stopped by closing the valve in the appropriate line **172***a*, **172***b* or **172***c* and the valve in the appropriate backwash outlet line, for example line **169***b*, is closed. The anion exchanger being regenerated is then vented to the atmosphere by means of a valve not depicted. Then, regenerating agent is flowed into the anion exchanger. For this purpose, a regenerating agent supply line **174** is provided, and it communicates respectively with anion exchangers **152***a*, **152***b* and **152***c* by means of valved lines **176***a*, **176***b* and **176***c*. The regenerating agent comprises alkali metal hydroxide, for example, potassium or sodium hydroxide or mixtures thereof. Preferably, the regenerating agent comprises sodium hydroxide utilized in aqueous solution at a concentration of 10% by volume. The alkali metal hydroxide reacts with the resin to provide resin in the hydroxide form and release anions containing hexavalent chromium and produce alkali metal salts containing hexavalent chromium in a negative radical, that is alkali metal chromates and dichromates. The amount of alkali metal hydroxide introduced is based on calculations of how much chromium entered and therefore is in a particular column with a sufficient amount being added so that when solution is removed from the column as described hereafter as the effluent of regeneration as defined hereafter, the effluent of regeneration will contain from about 90 to about 95% of the hexavalent chromium in the column just prior to initiation of regeneration. When the appropriate amount of regenerating agent has been introduced, flow of such into the column is stopped, and liquid is forced from the column utilizing a pressurized air purge. The pressurized air for the air purge is supplied through line **170**. When the air purge has forced the liquid from the column that readily is removed thereby, air introduction is continued and rinse water is simultaneously routed into the column for a predetermined time and is forced therefrom by the pressurized air. Rinse water flow is provided through piping described below. The streams leaving the column both as a result of purging of liquid in the column from addition of regenerating agent and as a result of purging liquid from the rinse water introduction make up the effluent of regeneration. These streams leave the columns **152***a*, **152***b* and **152***c* respectively through exit lines **178***a*, **178***b* and **178***c*. Thus, alkali metal hydroxide is introduced to provide an aqueous effluent from the column containing cations and from aboout 90 to about 95% of the hexavalent chromium present in a column just prior to initiation of regeneration and to leave in the anion exchange column the remainder of the cations and hexavalent chromium. Preferably, the amount of hexavalent chromiun removed from the column in the effluent is about 95% of that present just prior to initiation of regeneration.

The exit lines **178***a*, **178***b* and **178***c* communicate respectively with three-way valves **180***a*, **180***b* and **180***c*. During forcing of effluent of regeneration from a column, the appropirate three-way valve is positioned so as to route liquid into a respective communicating line **182***a*, **182***b* or **182***c*. The lines **182***a*, **182***b* and **182***c* communicate with a main line **184.**

After the effluent of regeneration has left the column being regenerated and has been routed to line **184,** the pressurized air supply is stopped by closing of the valve in the appropriate line **172***a*, **172***b* or **172***c*, but water introduction is continued to fill the column and simultaneously with the shutting off of the air supply the appropriate three-way valve **180***a*, **180***b* or **180***c* is repositioned so as to connect the respective line **178***a*, **178***b* or **178***c* into a recirculation loop described below. Piping for this water introduction as well as the rinse water introduction to provide part of the effluent of regeneration comprises a main water line **186** which in turn communicates with valved branch lines **188***a*, **188***b* and **188***c* which respectively communicate with cation exchanger entrance lines **190***a*, **190***b* and **190***c* with **188***a* and **190***a* being associated with exchanger **150***a*, **188***b* and **190***b* being associated with exchanger **150***b* and **188***c* and **190***c* being associated with exchanger **150***c*. The piping for the water addition system also includes a pipe **192***a* connecting exchangers **150***a* and **152***a*, a pipe **192***b* connecting exchangers **150***b* and **152***b*, a pipe **192***c* connecting exchangers **150***c* and **152***c;* the pipes **192***a*, **192***b* and **192***c* each contain valves which are not depicted. Thus, in introducing water into anion exchanger **152***a*, the water from main line **186** enters valved line **188***a* and then line **190***a*, then passes through cation exchanger **150***a*, then through line **192***a* and into anion exchanger **152***a* to fill the same. The exchangers **152***b* and **152***c* are filled with water in corresponding fashion when they are in a regeneration cycle. The passage of the water through the cation exchanger before entry into the anion exchanger provides the advantage of removing cations therefrom including divalent cations such as calcium and magnesium ions so that service water can be utilized without danger of hardness in the water clogging the exchanger system. In other words, the water can be drawn from a source of water containing divalent cations (for example, calcium and magnesium ions) since these cations are re-

moved prior to entry of the water into the anion exchanger.

Once the anion exchange column has been filled with water, water addition is stopped by closing the valve in the appropriate line **188***a*, **188***b*, **188***c*, the appropriate vent valve is closed, and recirculation between the anion exchange column and its associated cation exchange column is started. The recirculation loop including ion exchange columns **150***a* and **152***a* consists of line **178***a*, a line **194***a* containing a pump **196***a*, valve **180***a* joining lines **178***a*, **182***a* and **194***a* and positioned to provide flow between lines **178***a* and **194***a*, line **190***a* communicating at its upstream end with the downstream end of line **194***a*, and line **192***a*. The recirculation loop including ion exchange columns **150***b* and **152***b* consists of line **178***b*, a line **194***b* containing a pump **196***b*, valve **180***b* joining lines **178***b*, **182***b* and **194***b* and positioned to provide flow between lines **178***b* and **194***b*, line **190***b* communicating at its upstream end with the downstream end of line **194***b*, and line **192***b*. The recirculation loop including ion exchange columns **150***c* and **152***c* consists of line **178***c*, a line **194***c* containing a pump **196***c*, valve **180***c* joining lines **178***c*, **182***c* and **194***c* and positioned to provide flow between lines **178***c* and **194***c*, line **190***c* communicating at its upstream end with the downstream end of line **194***c*, and line **192***c*. To carry out recirculation, the appropriate pump **196***a*, **196***b* or **196***c* is operated. Recirculation is carried out between the anion exchanger and the cation exchanger in a loop until anions including the hexavalent chromiun containing anions in the anion exchanger being treated react with the anion exchanger resin in that exchanger and cations react with the resin in the cation exchanger. Conductivity sensors **198***a*, **198***b* and **198***c* are provided respectively sensing in lines **178***a*, **178***b* and **178***c* to indicate when reaction has been completed.

After reaction has been completed, recirculation is stopped by stopping the appropriate pump **196***a*, **196***b* or **196***c*.

Preferably, the regeneration cycle including backwashing, air purging, introduction of regenerating agent, removal of resulting solution, introduction of rinse water and removal of resulting solution, introduction of water and recirculation is carried out automatically so that the various valves including the valves in lines **188***a*, **188***b*, **188***c*, **158***a*, **158***b* and **158***c*, **169***a*, **169***b* and the valves **180***a*, **180***b* and **180***c* are operated automatically in accordance with a predetermined schedule.

The liquid passing through line **184** comprises an aqueous solution containing cations (alkali metal ions from the regenerating agent for the anion exchange zone) and a concentration of hexavalent chromium in the form of anions substantially higher than the relatively low concentration leaving compartment **98** or in tank **132.** It flows into a holding tank **200.** Intermittently liquid is pumped from tank **200** by pump **202** through a valved line **204** through a cation exchange column **206** referred to hereafter as cation exchanger **206,** exchanger **206** and column **206** (see FIG. 1A). Effluent from the cation exchanger passes into plater solution storage tank **32** via a line **208.** When the liquid passes through the cation exchanger **206,** cations in the liquid react with a resin in the exchanger and are exchanged for hydrogen ions, and the effluent from the cation exchanger is an aqueous solution of chromic acid containing, for example 10 to 50 grams per liter of chromic acid expressed as CrO_3, that is an acidic aqueous solution comprising a concentration of hexavalent chromium in the form of anions substantially higher than the concentration of such in the stream leaving compartment **98** through line **126** or in tank **132.** Meters **210***a* and **210***b* (pH meters) are provided on either side of exchanger **206** for the easy determination of whether the resin bed in exchanger **206** is depleted, that is whether the resin in the exchanger is spent and needs to be regenerated.

The ion exchange resin utilized in cation exchanger **206** is of strong acid type and is used in the hydrogen form. It contains sulfonic acid functional groups in a polymer matrix and is prepared, for example by the nuclear sulfonation of styrene-divinylbenzene. The resin utilized is highly resistant to oxidation because the concentration of chromic acid to which the column is exposed is such as to be highly oxidative. The resin contains a relatively high level of cross-linking to provide such oxidation resistance. A suitable resin is sold under the tradename Amberlite 200 by Rohm and Haas; this resin is sold in the sodium form and is converted to the hydrogen form for use.

The solution leaving compartment **98** through line **126** contains, for example, 0.1 to 0.3 grams per liter of chromic acid expressed as CrO_3 and the solution leaving the exchange system through line **208** contains for example 10 to 50 grams per liter of chromic acid expressed as CrO_3. Thus, the ion exchanger system serves to concentrate the chromic acid solution so that is can be treated as described hereafter so as to be suitable for reuse in the plater tanks.

An evaporation system is provided to control the volume of liquid in the system and to remove water from the system inasmuch as liquid from line **94** comprises chromic acid at a concentration of, for example, 85 to 100 grams per liter of chromic acid expressed as CrO_3 and the liquid from line **208** has a concentration of chromic acid expressed as CrO_3 of, for example, 10 to 50 grams per liter. In other words, the water added via line **76** and the excess water added into the system through line **174** has to be removed to concentrate solution to plating strength. The evaporation system comprises an evaporator **211** defining an evaporation zone where solution is heated against steam passing in indirect heat exchange relation as indicated by lines **212***a*, and **212***b*. The evaporator has a concentrated liquid exit line **214** and a vapor exit line **216.** Also communicating with the evaporator is a liquid feed line **218** containing a pump **220** and a valve **222** and communicating at its upstream end with the bottom of plating tank **32.** In utilizing the evaporator, solution from plater storage tank **32** is passed from the plater storage tank to the evaporator and concentrated solution is passed from the evaporator to the plater storage tank. More particularly, the liquid is pumped by pump **220** from the lower portion of plater storage tank **32** through line **218** into the evaporator where is is heated indirectly against steam passing as indicated by lines **212***a* and **212***b* and subjected to vacuum whereby water is flashed off leaving through line **216** (such water is condensed and disposed to waste) and concentrated liquid leaves the evaporator via line **214** and is fed back into plater storage tank **32.**

An inventive concept herein concerns the addition of regenerating agent to provide an effluent containing

from about 90 to about 95% of the hexavalent chromium present in the anion exchange resin just prior to initiation of regeneration and then recirculating the remaining 5 to 10% hexavalent chromium and reacting it with the anion exchange resin to establish a continuing level of hexavalent chromium in the resin. This procedure maximizes the concentration of hexavalent chromium in the solution flowing into tank **200** from line **184.** Once the 5 to 10% level of hexavalent chromium is established in the resin, additional chromium need not be utilized to establish this level during the life of the resin; therefore, the establishment of this level is provided with minimum usage of hexavalent chromium. Thus, this concept enables maximizing hexavalent chromium concentration as a result of ion exchange with the expenditure of only an insubstantial amount of hexavalent chromium to accomplish this.

The above inventive concepts are illustrated in the following specific example.

EXAMPLE

The system of FIGS. 1A and 1B is utilized. The system is generally operated as described above. The specifics are presented below.

Steel strip (36 inch width) having been preliminarly treated in electrolytic cleaning and pickling steps is passed through the system. Chrome plating is applied in tanks **12, 14, 16** and **18.** Objectionable oxide coating is removed in tank **20.** The plated strip is washed in tanks **52** and **54.** In tank **56,** hexavalent chrome oxide coating is applied. In tank **58** the strip is washed. Finally the strip is further washed in spray washer **96.** The strip exiting from washer **96** is ready for drying. The line speed is 1,550 feet per minute.

Each of the tanks **12, 14, 16, 18** and **20** contains 1,700 gallons of plater solution. The plater solution is an aqueous solution comprising 150 grams per liter of chromic acid expressed as CrO_3, 1 gram per liter of sulfuric acid expressed as SO_4 and 3 grams per liter of metal silicofluorides expressed as SiF_6. 100 gallons per minute of plater solution enters each tank and 100 gallons per minute of plater solution leaves each tank. Of the 100 gallons per minute entering tank **12,** 2 gallons per minute enters through prewet sprays **19.** The temperature of the plater solution is 115°.

Tank **52** contains 800 gallons of aqueous solution containing about 90 grams per liter of chromic acid expressed as CrO_3. Solution enters and leaves tank **52** at the average rate of about 1.5 gallons per minute.

Tank **54** contains 1,700 gallons of aqueous solution containing about 35 grams per liter of chromic acid expressed as CrO_3. Solution enters and leaves tank **54** at the average rate of about 1.5 gallons per minute.

Tank **56** contains 1,700 gallons of aqueous solution containing chromic acid at a concentration of about 35 grams per liter expressed as CrO_3, 0.15 grams per liter of sulfuric acid expressed as SO_4 and 0.6 grams per liter of metal silicofluorides expressed as SiF_6. Solution passes in and out of tank **56** at a rate of approximately 150 gallons per minute. The temperature of solution in tank **56** is 120°.

Tank **58** contains 800 gallons of aqueous solution. This solution has a concentration of chromic acid expressed as CrO_3 of 10 grams per liter. 1.5 gallons per minute of solution continuously pass in and out of this tank.

In washer **96** 20 gallons per minute of demineralized water enters through sprays **104***c;* 20 gallons per minute overflows from compartment **104** to compartment **102;** 20 gallons per minute is sprayed by sprays **102***c;* 20 gallons overflows from compartment **102** to compartment **100;** 20 gallons per minute is sprayed through sprays **100***c;* 20 gallons per minute overflows from compartment **100** to compartment **98;** 20 gallons per minute is sprayed through sprays **98***c;* and 20 gallons per minute leaves through line **126.** the water entering through sprays **104***c* is at a temperature of 180°. The use of water at this temperature aids in strip washing and drying.

The solution leaving through line **126** has a concentration of chromic acid expressed as CrO_3 of 0.2 grams per liter. The concentration of chromic acid expressed as CrO_3 in compartment **104** is in low parts per million. The strip leaving washer **96** contains trace or no amounts of chromic acid.

Tank **132** is a 6,000 gallon tank and controller **138** operates valve **140** to maintain a continuous stream of liquid through pipe **134.** This stream of liquid is an aqueous solution having a concentration of hexavalent chromium in the form of anions expressed as CrO_3 of 0.2 grams per liter.

The heat exchanger **142** operates to cool the solution from pipe **134** to 100°.

The solution having been so cooled is routed to two of the three cation exchangers **150***a*, **150***b* and **150***c*. These exchangers and each of the other ion exchangers in the system are 10 feet high and 54 inches in diameter and of the conventional type where the ion exchange resin is maintained upon a screen which is positioned in the bottom of the exchanger, the exchanger is vertically oriented and the solution to be treated enters the top and leaves the bottom. The ion exchange resin utilized in the exchangers **150***a*, **150***b* and **150***c* is Amberlite IR-120 Plus, and it is utilized in the hydrogen form.

The effluent from the two cation exchangers (of **150***a*, **150***b* and **150***c*) that are on stream is passed to the two anion exchangers which communicate with such cation exchangers. The anion exchangers **152***a*, **152***b* and **152***c* contain as an ion exchange resin Amberlite IRA-900. This resin is supplied in the chloride form and is converted to the hydroxide form for use.

The effluent from the anion exchangers is demineralized water which is routed to storage tank **162.**

Every eight hours one set of cation and anion exchangers is taken out of the line and a fresh set of cation and anion exchangers is put in the line. For example, if cation exchangers **150***a* and **150***b* and anion exchangers **152***a* and **152***b* are being utilized and the resin in exchangers **150***a* and **152***a* is the most depleted, exchangers **150***a* and **152***a* are taken out of the line and exchangers **150***c* and **152***c* are put in the line.

The cation exchanger taken out of the line is regenerated prior to regenerating the associated anion exchanger. The regeneration comprises backwashing, then treating with a regenerating agent consisting of 10% aqueous sulfuric acid and then rinsing. Flow rates and times are in accordance with the resin manufacturer's recommendations.

The anion exchanger which is taken out of the line is regenerated first by backwashing for 10 minutes utilizing service water having cations removed therefrom introduced through the appropriate backwash water introduction line. When the ten-minute time period has

ended, the valve in the backwash water line is closed automatically; then the appropriate valve in the air purge line (that is, the valve in the appropriate branch line **172***a*, **172***b* or **172***c*) is automatically opened and the residual backwash water is forced from the anion exchanger through the appropriate backwash water outlet line. After the valve for air purging has been open for 10 minutes, it automatically closes and the anion exchanger is automatically vented to the atmosphere.

Then the valve in the appropriate regenerating agent introduction line **176***a*, **176***b* or **176***c* automatically opens. The regenerating agent utilized is aqueous sodium hydroxide solution containing 10% sodium hydroxide by volume. Four hundred gallons of regenerating agent is introduced over a 40 minute time period. At this point, the valve in the regenerating agent introduction line automatically closes, and the valve in the appropriate line **172***a*, **172***b* or 172*c* automatically opens and the appropriate three-way valve **180***a*, **180***b* or **180***c* is automatically positioned to route liquid to tank **200.** After 10 minutes, the air has forced substantially all of the liquid from the column being regenerated. At this point the valves in the appropriate lines **188***a*, **188***b*, **188***c*, **192***a*, **192***b*, **192***c* automatically open whereby water passes through a cation exchanger and then into the anion exchanger which is being regenerated. The water is introduced at the rate of 60 gallons per minute. After 1 minute, the appropriate valve is closed to shut off the air. The 60 gallons of water introduced before the air is shut off serves to rinse out residual solution heavily laden with chrome, and carry it to tank **200.** The 460 gallons routed to tank **200** contain 95% of the hexavalent chromium which was in the resin in the column just prior to initiation of regeneration.

When the air is shut off, the appropriate three-way valve **180***a*, **180***b* or **180***c* is automatically repositioned to recirculation position (that is, to provide communication, for example between lines **178***a* and **194***a*) and water introduction is continued to fill the column. Then water introduction is automatically stopped by means of a conductivity switch, the vent valve closes and the appropriate pump **196***a*, **196***b* or **196***c* is automatically started and recirculation between the anion exchanger being regenerated and its associated cation exchanger is carried out. This recirculation is continued until the conductivity cell **198***a*, **198***b* or **198***c* registers 25 micromhos thereby indicating reaction of the sodium chromates and dichromates with the resins to establish a level chromate and dichromate in the anion exchange resin.

Except during regeneration of column **206,** solution is pumped by pump **202** from tank **200** through exchanger **206.** The exchange resin in this exchanger is Amerlite 200 which has been converted to the hydrogen form; it is much more highly oxidative resistant than the cation exchange resin Amberlite IR-120 Plus utilized in the cation exchangers **150***a*, **150***b* and **150***c*. Passage of the solution through the cation exchange resin removes cations and the effluent from the cation exchanger **206** is aqueous chromic acid solution containing 25 grams of chromic acid per liter expressed as CrO_3. The differential pH as indicated by meters **210***a* and **210***b* indicates resin bed depletion, and a predetermined higher pH being registered by meter **210***a* indicates that the resin bed is ready to be regenerated. Regeneration is carried out utilizing backwashing, introduction of regenerating agent and rinsing in accordance with the manufacturer's directions for the particular resin being utilized. The regenerating agent utilized is 10% by volume aqueous sulfuric acid.

Tank **32** contains about 6,000 gallons when the line tanks are full.

Recirculation is carried out between tank **32** and evaporator **211** with 70 gallons per minute being pumped by pump **200** whereby the concentration of solution in tank **32** is maintained at 150 grams per liter of chromic acid expressed as CrO_3. Steam is introduced through line **212***a* to supply heat. A vacuum of 26 inches of Hg is utilized in evaporator 211; this vacuum is provided by an eductor on line 216.

The recirculation through lines **44** and **46** between heat exchanger **42** and tank **32** is at the rate of 500 gallons per minute and cooling water is passed through exchanger **42** via lines **50***a* and **50***b* countercurrent to the flow of plater solution to remove heat from the system and maintain the temperature of the plater solution at 115°F.

The use of different cation exchangers for the cation exchange upstream of the anion exchange and for the cation exchange downstream of the anion exchange allows the use of different cation exchange resins so that a highly oxidative resistant resin can be utilized in exchanger **206** where such resin is desirable because of the relatively high concentration of hexavalent chromium in the form of anions while a resin which is not highly oxidative resistant but which is less expensive can be utilized in exchangers **150***a*, **150***b* and **150***c* where the concentration of hexavalent chromium in the form of anions is lower and less oxidation resistance is needed. Thus, the use of different cation exchangers and different resins significantly contributes to the economy of the system. The removal of only 95% of the hexavalent chromium from the anion exchangers **152***a*, **152***b* and **152***c* during regeneration maximizes the concentration of chromic acid in the effluent of regeneration thereby significantly contributing further to the economy of the system by reducing the load on the evaporation system. Finally, the recirculation between the plater tanks and tank **32** in combination with adding the streams from lines **94** and **208** into tank **32** and treating solution from tank **32** in the evaporator provides significantly more accurate plater solution volume and concentration control than if streams **94** and **208** were passed directly to an evaporator and has the further advantage of allowing continuous evaporator operation on a relatively large volume of liquid compared to the volume of the streams from **94** and **208** thereby permitting continuous evaporator operation without danger of exceeding the flash point of the solution being treated.

The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. Therefore, in view of the variations that are readily understood to come within the limits of the invention, such limits are defined by the scope of the appended claims.

What is claimed is:

1. Method both for recovering chromium from strong base anion exchange resin which has been used in the hydroxide form to remove hexavalent chromium in the form of anions from a solution and for regenerating the resin for reuse for removing hexavalent chromium in

the form of anions from a solution; comprising the steps of

a. introducing water into a column containing the resin thereby backwashing the resin to remove extraneous solids and resin fines,

b. removing residual backwash water,

c. passing aqueous alkali metal hydroxide into the column containing the resin and providing effluent from the column containing from about 90 to about 95% of the hexavalent chromium present in the column while leaving in the column alkali metal cations and the remainder of the hexavalent chromium in the form of anions to thereby optimize the concentration of hexavalent chromium in the effluent,

d. introducing water into the column and recirculating resulting liquid between that column and a column containing cation exchange resin of the strong acid type in the hydrogen form to react hexavalent chromium in the form of anions with the anion exchange resin and to react the alkali metal cations with the cation exchange resin, to establish a continuing 5 to 10% level of hexavalent chromium in the anion exchange resin thereby conserving chromium.

2. Method as recited in claim **1,** in which the alkali metal hydroxide is sodium hydroxide.

3. Method as recited in claim **1,** in which in step (*b*) residual backwash water is removed utilizing pressurized air.

4. Method as recited in claim **3** in which liquid resulting in the column containing the anion exchange resin from passing aqueous alkali metal hydroxide thereinto is removed from the column utilizing pressurized air.

5. Method as recited in claim **4** in which subsequent to the removal of liquid resulting in the column containing the anion exchange resin from passing aqueous alkali metal hydroxide thereinto and prior to step (*d*), rinse water is introduced into that column and resulting solution is removed utilizing pressurized air to provide a portion of the effluent of step (*c*).

6. Method as recited in claim **5** in which the rinse water and pressurized air are introduced into the column containing the anion exchange resin simultaneously.

7. Method as recited in claim **1** in which the water introduced in step (*d*) is passed through a column containing cation exchange resin of the strong acid type in the hydrogen form prior to such introduction

8. Method as recited in claim **1** wherein in step (*c*) the effluent contains about 95% of the hexavalent chromium.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,885,018 Dated May 20, 1975

Inventor(s) Robert B. Smith

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 19, "1000" should read -- 1005 --.

Column 2, line 17, "50" should read -- so --.

Column 16, line 9, "200" should read -- 220 --.

Signed and Sealed this

twenty-third Day of *September 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
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