

Dec. 2, 1969

L. E. LANCY

3,481,851

APPARATUS AND PROCEDURE FOR RECONDITIONING
METAL TREATING SOLUTIONS

Original Filed Nov. 16, 1964

4 Sheets-Sheet 1

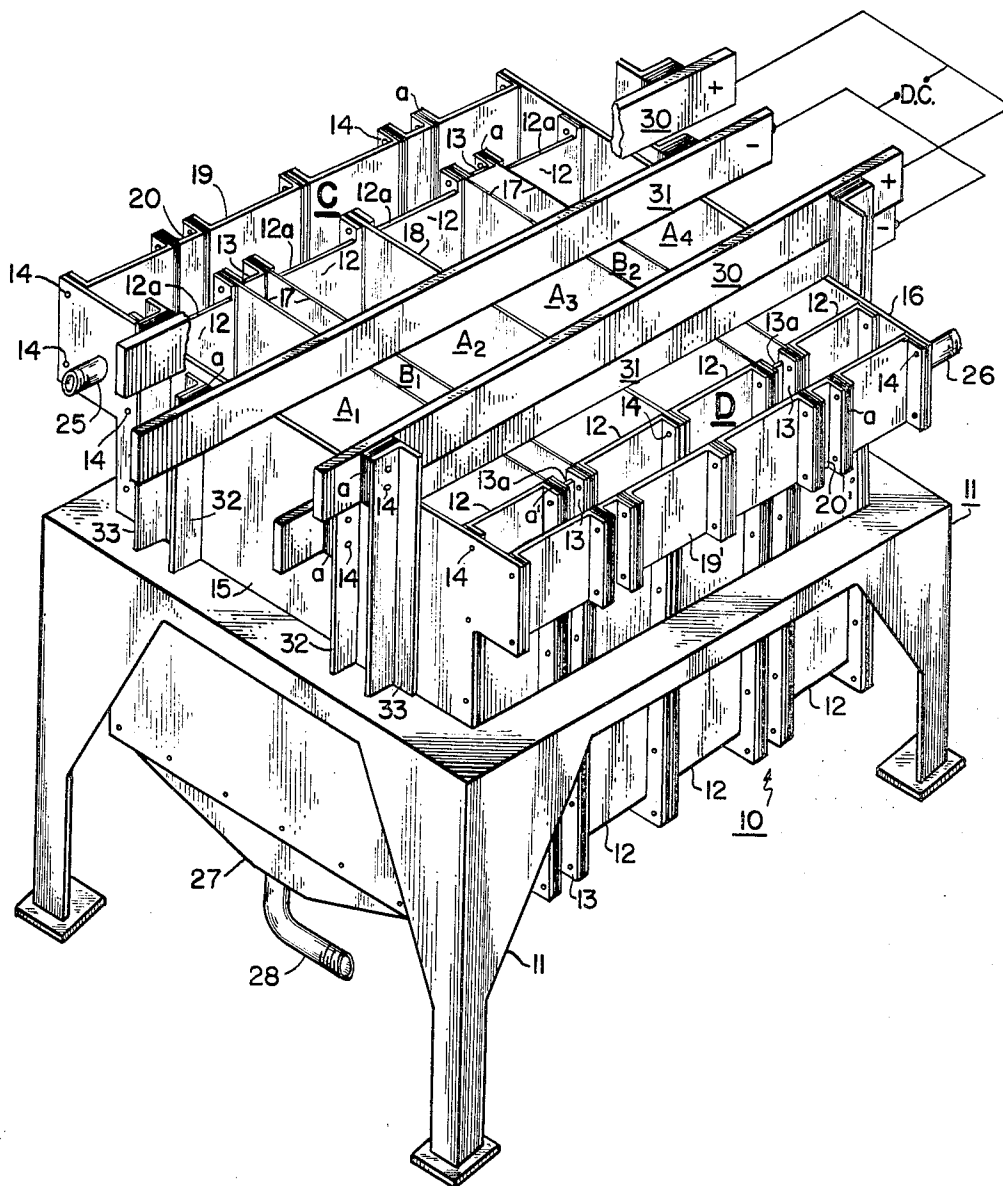


Fig. 1

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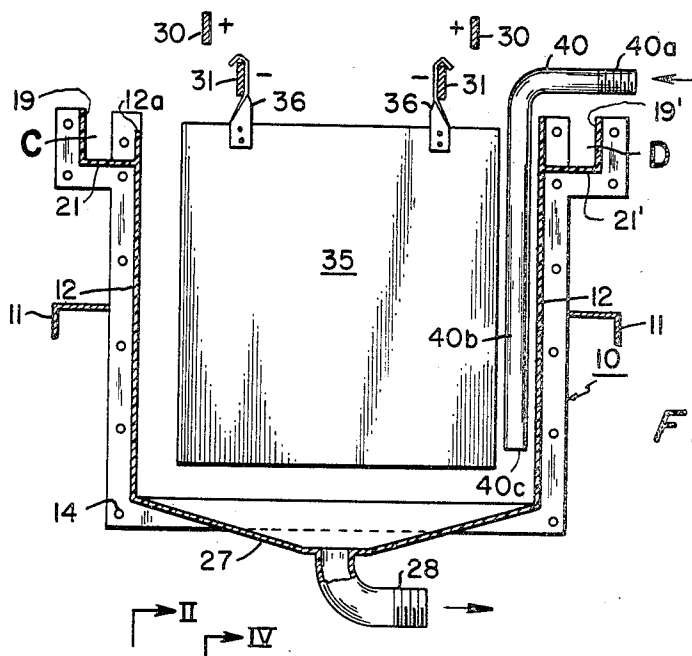


Fig. 2

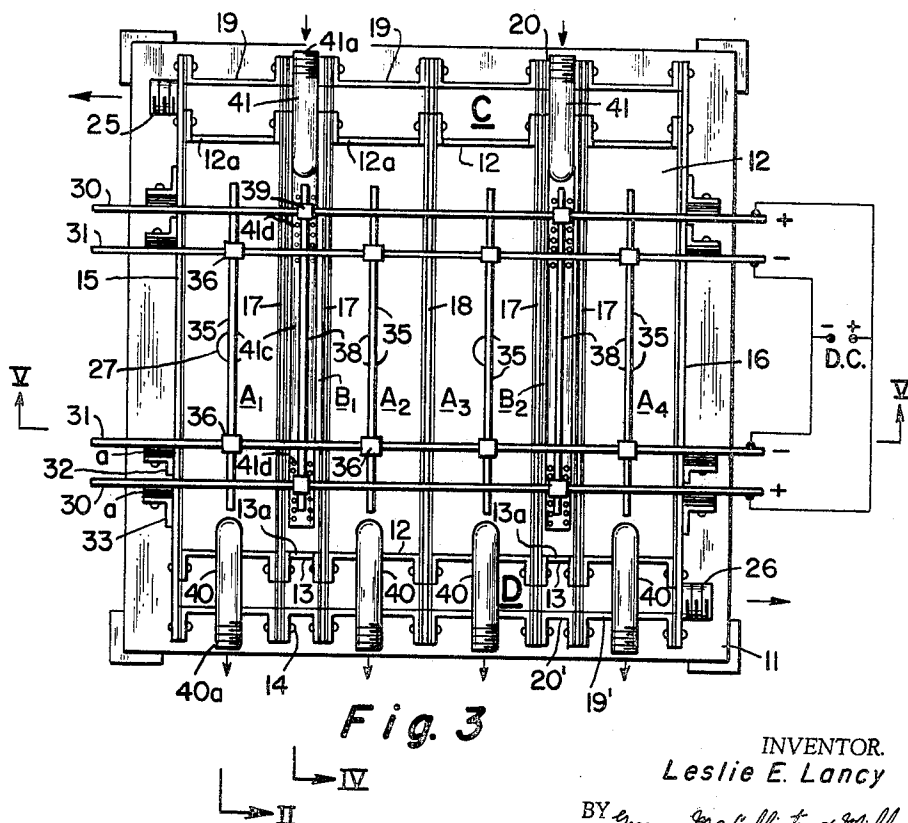


Fig. 3

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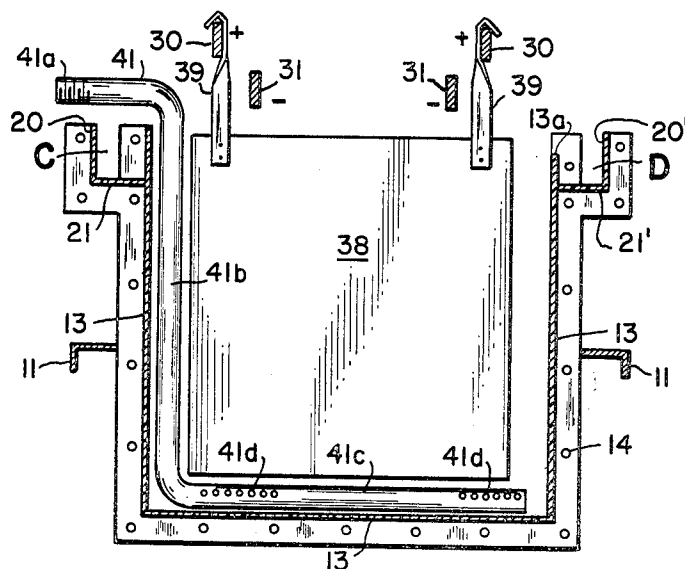


Fig. 4

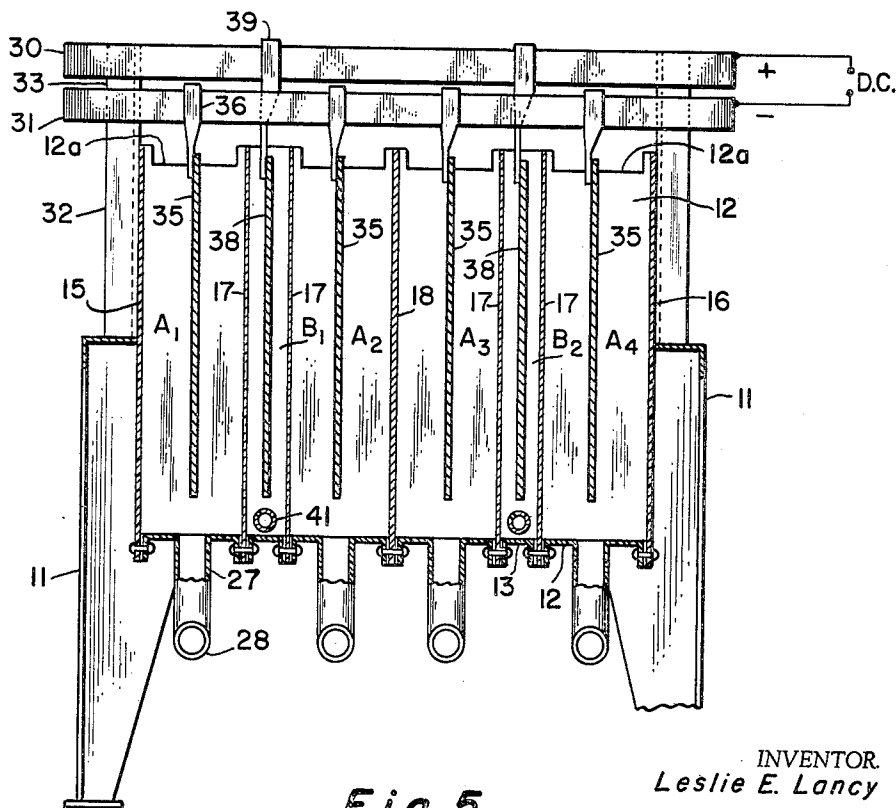


Fig. 5

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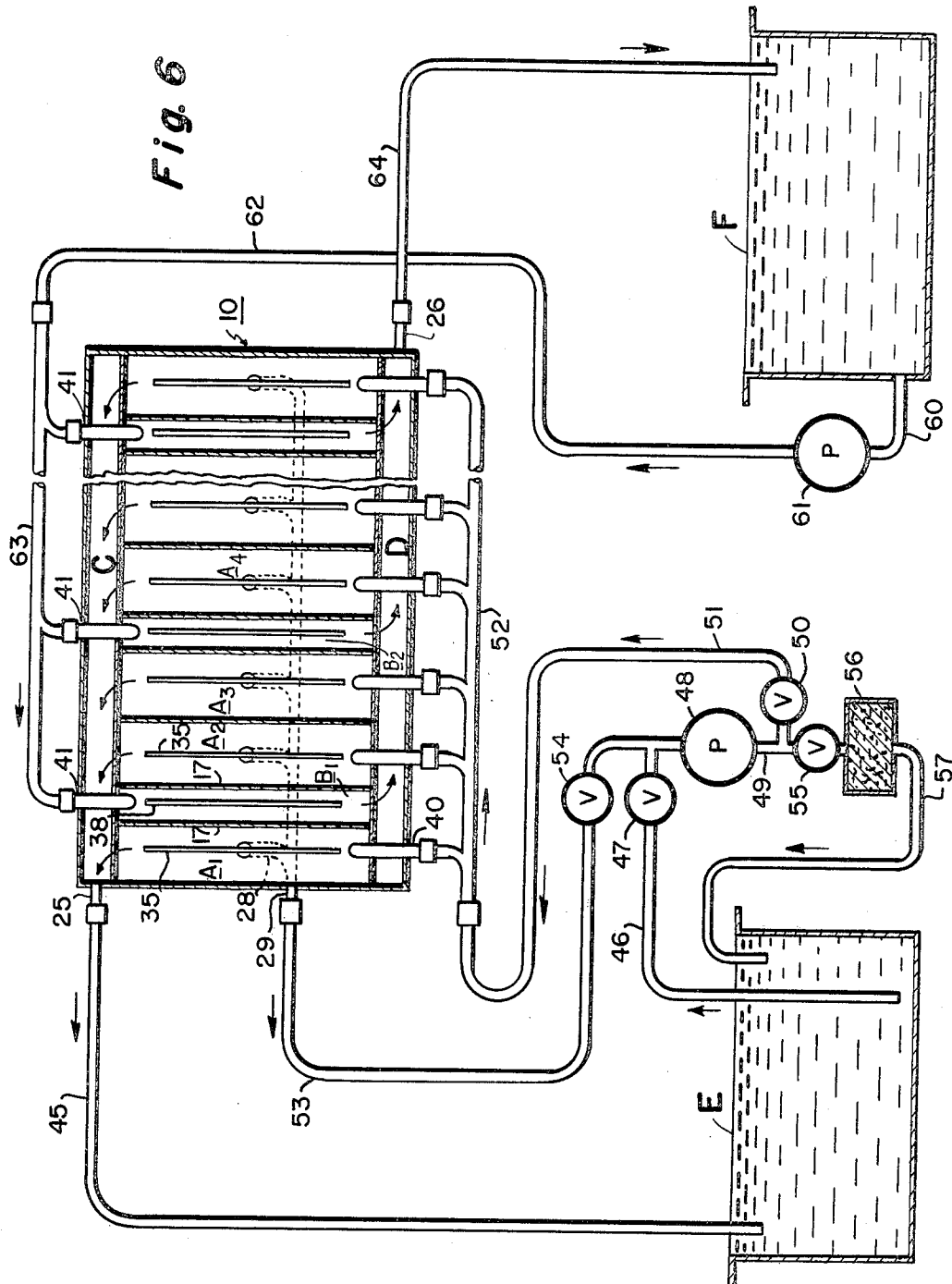
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APPARATUS AND PROCEDURE FOR RECONDITIONING METAL TREATING SOLUTIONS

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Continuation of application Ser. No. 411,305, Nov. 16, 1964. This application Jan. 10, 1969, Ser. No. 797,327

Int. Cl. C23g 1/32

U.S. Cl. 204—180

19 Claims

ABSTRACT OF THE DISCLOSURE

Electrodialysis procedure and apparatus are employed for reconditioning a used chromic acid containing metal treating solution that is out of condition due to the presence of trivalent chromium and dissolved foreign metals therein. The used solution is introduced as an anolyte solution into an anode compartment of an electrodialysis cell, an acid catholyte solution is introduced into a cathode compartment, a cation permeable membrane is placed between the compartments, the cell is electrically energized, the dissolved foreign ions of the class consisting of copper, iron, zinc, nickel and cadmium are selectively passed through the membrane into the catholyte solution, the chromium ions are restricted from passing through the membrane, and simultaneously with the passage of the dissolved metals, oxygen evolved at the anode reoxidizes trivalent chromium in the anolyte solution into hexavalent chromium. The anolyte solution may then be removed from the cell for reuse in metal treating operations.

This application is a continuation of application No. 411,305 of Nov. 16, 1964, now abandoned, entitled Apparatus and Procedure for Reconditioning Metal Treating Solutions.

This invention deals with the treatment of chromic acid solutions, such as pickling and acid bright solutions in order to reconstitute or recondition them and, particularly, to procedure and apparatus for converting trivalent chromic acid into hexavalent chromic acid and simultaneously therewith removing contaminating metals. A phase of the invention deals with procedure and apparatus for continuously reconditioning chromic acid containing solutions, in order that an electrolytically efficient solution may be maintained at all times.

In the metal finishing industry, it has been customary to use chromic acid basis solutions, since it is a highly oxidizing acid suitable for chromium plating and acid brightening or pickling of other metals. In chromium plating, a solution of about 18 to 40 ounces per gallon is used with minor addition agents, usually in a total concentration of not more than about 1% of the chromium acid content. Chromic acid pickling and brightening acid solutions contain major amounts of chromic acid from about 2 ounces per gallon to about 32 ounces per gallon, and also usually contain some additional acids to accelerate or retard the dissolution rate of the various metals for which the chromic acid in solution form is employed for its solvent action. In all of these processes, I have found that the amount of metal concentration progressively increases and is detrimental in its effects.

(A) PLATING SOLUTIONS

A chromium plating solution mainly deteriorates due to two natural conditions in the process. In the first place, the hexavalent chromium is continuously reduced on the cathode to a trivalent state from which chromium metal is deposited on the cathode. Ordinarily, a greater amount of hexavalent chromium is reduced on the cathode than is incorporated in the deposit. The cathode efficiency of the chromium deposit is not more than about 10 to 18%. Most of the trivalent chromium that is reduced on the cathode surface is again reoxidized on the anode surface. In certain processes, especially when the anode area is relatively small or confined, such as when tubing or cylinders are being internally plated or when the balance of trivalent chromium cannot be maintained due to high current density and product requirements, the trivalent chromium concentration continuously increases and becomes detrimental for the plating process above about 5 to 6% of the hexavalent chromium concentration.

Although it is possible to regenerate a chromium plating solution by low current density electrolysis by using as large an anode area as possible or by enclosing the cathode in a porous diaphragm or container to keep hydrogen out of the electrode and allow the passage of current and thus improve the otherwise low efficiency of reoxidation of the trivalent chromium on the anode surface, such procedures are quite cumbersome and expensive and are seldom used. Also, I have determined that the chromium plating installation provides an inefficient container and system for such procedures. Further, the factor of the slow build-up of foreign metal ions in the chromium plating solution cannot be met by such procedures.

The second factor contributing to the deterioration of a chromium plating solution is the slow build-up of foreign metal ions therein. Foreign metal is usually anything that is not purposely added to the solution that basically should contain only ions of the chromium metal. Foreign metal ions may be metals in the nature of copper, zinc, iron, nickel, etc. I have found that chromic acid has excellent solvent action on zinc and copper and a lesser action on iron and nickel.

The build-up of metal impurities in the solution is due to the particular metal, such as copper or zinc, falling into the solution. For example, if the plating rack is made of a cuprous alloy, it will be attacked during the plating process and dropped into the solution, or die-cast zinc metal will slowly dissolve in the bottom of the plating tank. Nickel contamination is usually caused by the drag-in of nickel sulfate solution from a previous nickel plating process. Iron contamination or buildup is caused by the slow attach on the internal surfaces of steel parts, such as tubular metal that is bare; such iron is continuously attacked by the chromium plating solution while outside areas are under cathodic protection and are receiving the plating deposit. Trivalent chromium and iron reduce the conductivity of the plating solution and the higher concentrations tend to interfere with the throwing power and the bright plating of the process. On the other hand, zinc, nickel and copper tend to produce a haze or lack of luster on the plated surface, a lack of covering power on recessed areas, and a reduced throwing power in recesses. A reduced efficiency in deposition is also noted.

The only known method for removing metallic impurities from a chrome plating solution has been to treat

it on an ion exchange resin bed. This requires considerable dilution of the plating solution to avoid oxidizing the organic resin. The purification is effected through the resin bed, and thereafter the plating solution must be reconcentrated through evaporation in order to obtain the same solution concentration as existed before the treatment. In view of the limited capacity of the ion exchange resin, very large ion exchange surfaces are required to process even 300 to 400 gallons of the chromium plating solution which is considered a small installation in today's practice. I have also found that the attack of the chromic acid on the bed, even using a four-fold dilution, is quite severe and that after four or five applications, a considerable impairment is evident on the exchange capacity of the resin. It should be recognized that usual metal removal techniques, such as electrolysis and precipitation, cannot be utilized for chromium plating solutions.

From the above, it will be evident that the dual factors which enter into the deterioration of a chromium plating solution have not heretofore been capable of being effectively, efficiently and inexpensively met by individual processing treatments. The desideratum is to provide a treatment process or apparatus system which will enable both factors to be met simultaneously as well as efficiently, effectively and inexpensively.

(B) PICKLING SOLUTIONS

Many bright pickling solutions called bright dips contain a major proportion of chromic acid in their make-up, due to its excellent solvent action on metals, and also due to the viscosity of a chromic acid type of film. The solution usually contains various inorganic acids and sometimes, organic acids or neutral salts, to provide a balanced formulation. Such a formulation is selected to give the right solvent and inhibiting action as well as viscosity for a preferred rate of dissolution of the metal, and is specifically prepared for each particular metal and the rate of removal desired. In such bright acid dips or bright acid pickles, the chromic acid serves the same purpose, namely, that of an oxidizing acid having a good solvent action and leading to the forming of a viscous film on the metal surfaces. The latter property is due to the viscosity of the chromic acid, itself, and the even higher viscosity of metal chromate complexes.

The most common of the bright acid pickles, namely for copper and copper alloys, are usually sulfuric acid based. Sometimes, they additionally contain sodium chloride or fluorides or additional organic acids to enhance the viscous nature of the solution. Bright dipping and chromate conversion film providing solutions for zinc, cadmium, aluminum and manganese usually contain a lower concentration of chromic acid of from about 2 to 32 ounces. The concentration will depend on the metal being treated, the rate of metal dissolution desired, and the concentration of thickness of the chromic acid film that is to be left on the metal surface undergoing treatment.

Chromic acid type stripping solutions are popular due to their selective solvent action on some metals and their inhibiting reaction towards the dissolution of other metals. For example, copper coatings may be stripped from steel without attacking the basis or backing metal. An aluminum oxide surface may be stripped from aluminum without attacking the basis metal. Also chromic acid is used for anodic electrolytic processing of zinc, aluminum and magnesium, in view of its inhibiting action on the metal surface as an oxide film is established.

In all these metal finishing processes employing chromic acid as the common element, deterioration of the solution is caused by two factors. The first factor is due to the enrichment of the metal ions to which the process is applied. The other factor of deterioration is due to a slow conversion of the hexavalent chromium into trivalent chromium. This results from the oxidizing action of the solution on the metals in the course of which the chromic acid gives up electrons, and is, itself, reduced. As the

trivalent chromic acid concentration increases and the foreign metal ions in the solution build-up, the effectiveness of the process solution is progressively impaired. Thus, at certain concentrations of the metal ions or of the trivalent chromium, the solution will not perform its original function. At this time, the usual practice has been to waste or discharge the solution and make up a new one.

The wasting and the providing of a new solution is, at the present time, the only commonly available and economical means of keeping a plant in operation. It is expensive, since chromic acid salt is expensive (costing about \$.35 per pound), and also because the chromic acid is extremely toxic. Thus, meticulous and complete treatment of the waste solution is necessary before it can be discharged. I have determined that the waste treatment cost may be two or three times as high as the original cost of the chemical. However, treatment of toxic wastes has become a requirement in most localities and thus, the cost of the treatment chemicals and processing of the waste solutions must be added to the original cost of the chemicals entering into the working solution and the cost of the treatment employment of such a working solution.

In view of the above considerations, it has been an object of my invention to develop an apparatus, system or procedure for treating chromic acid containing solutions which will solve the problem above-presented by fully meeting the factors involved.

Another object of my invention has been to provide an apparatus, system or procedure that will effectively and efficiently, in one operation, meet all the factors entering into the problem and enable the renovation, reconditioning or reconstituting of a chromic acid treating solution so that it may be reused and not wasted.

A further object of my invention has been to develop an effective renewing procedure, in accordance with which a chromic acid containing solution may be continuously renewed for effective reuse in such a manner as to conserve the chromic acid content thereof.

A still further object of my invention has been to provide a procedure for removing foreign metal ions from a chromic acid treating solution, and if desired, for recovering such ions.

These and other objects of my invention will appear to those skilled in the art from the illustrated embodiments and description thereof.

In the drawings,

FIGURE 1 is a perspective view in elevation of a solution reconstituting or renewing apparatus employing my invention;

FIGURE 2 is an end section in elevation of a cathode part or chamber of the apparatus of FIGURE 1 on the scale of and taken along the line II—II of FIGURE 3;

FIGURE 3 is a top plan view on the scale of and of the apparatus of FIGURE 1;

FIGURE 4 is a section in elevation on the scale of FIGURES 2 and 3 of an anode part or chamber of the apparatus of FIGURE 1 and taken along the line IV—IV of FIGURE 3;

FIGURE 5 is a side section in elevation on the scale of and taken along the line V—V of FIGURE 3; and,

FIGURE 6 is a somewhat diagrammatic system layout illustrating a system employing my invention as applied to a representative metal treating solution, in the nature of a plating or pickling solution, such as a copper pickling solution.

In solving the problem involved, I discovered that an electro dialysis approach to the factors involved could be employed, although heretofore it has only been used in electrochemical processing. In electro dialysis, a permeable membrane is inserted between positive and negative electrodes. When direct current power or energy is applied, electrically charged ions in the electrolyte will pass through the membrane to complete the electric circuit.

By employing various conventional substances for membrane material, it is possible to enrich, concentrate or deplete specific electrolytes on either side of the membrane. A commercially available membrane material containing a high percentage of cationic ion-exchange material will allow the passage of cations and, at the same time, will be impermeable or less permeable to anions. Conversely, a membrane containing a large colony of anion exchange resins will be permselective for anions. That is, cations having a positive charge will move towards the cathode, due to the attraction of the opposite electrical charge. Thus, a cation permeable membrane having negatively charged resin molecules will function as a cationic ion exchange membrane. The resin molecules are held together in a plastic film cast around them with sufficient porosity to allow intimate contact between the cationic resin and the solution, and thus leave a bridge open for the cations to move across the member, although hydraulically the membrane may appear to be impervious.

As shown in the drawings, I use a basic type of electrodialysis cell having two compartments, one holding the positive electrode and called the anode compartment and containing an electrolyte solution called the anolyte. The other or second compartment contains the negative electrode called the cathode and containing the catholyte solution which is separated from the other compartment by a membrane.

I have found that by using an electrodialysis cell technique, it is now possible to remove the detrimental ions, such as copper, zinc, nickel and iron, by passing them through a cation permeable membrane that separates or divides anolyte and catholyte parts or zones of the cell and that has good blocking properties for the anion, namely, the chromic acid. I use a catholyte having a solvent action for the metallic ions that are to be removed through the cation permeable membrane, using the electrolysis force of direct current energy applied to a cathode and an anode of the cell. The membrane will be kept free of pore plugging, and the dialysis action will not be impaired throughout a long time electrolysis process. I have experimentally operated uninterruptedly or continuously the same membrane for four weeks without blockage of its pores. This appears to be due to the good solvent action of the catholyte used for receiving the metallic ions that pass through the membrane.

I have discovered that with an anode electrode material, such as lead or a lead alloyed with antimony, tin or silver, only a small part of the trivalent chromium that behaves like a cation will pass through the membrane into the catholyte zone or compartment of a dialysis cell, and that a major portion of the trivalent chromium in the chromic acid plating solution will be reconverted on the anode surface to the desired hexavalent chromium. Thus, I have found that a regeneration of a used chromium plating solution in accordance with by electrodialysis approach will accomplish both a reconversion of the trivalent chromium to hexavalent chromium and a removal of foreign metal ions from the solution. The first action makes the hexavalent chromium again available, so that the solution may be reused when the foreign metal ions have been at least reduced below a minimal concentration. I have found that it is not necessary to completely remove the foreign metal ions from the solution, and that below a minimal concentration they are not detrimental. Allowing a foreign metal ion concentration to remain in the solution up to this minimal will tend to increase the efficiency of the electrodialysis process. Thus, I find that the operation of renovating the solution can be effectively and efficiently accomplished without endeavoring to completely remove the metallic impurities.

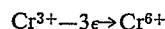
By way of example, I have treated a chromium plating solution that was badly out of condition, in the sense of containing an extremely high concentration of trivalent

chromium and of foreign contaminating metals, as indicated by the following analysis:

	G./liter
Hexavalent chromium, Cr^{6+} as CrO_3 -----	290.0
Trivalent chromium, Cr^{3+} as CrO_3 -----	66.5
Total chromium as CrO_3 -----	356.5
Zinc, Zn -----	6.85
Iron, Fe -----	18.5
Nickel, Ni -----	27.5
Copper, Cu -----	12.7

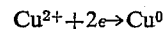
The above solution was electrolyzed in an electrodialysis cell containing a cation permeable membrane. The catholyte consisted of about 10% by volume of hydrochloric acid solution with a stainless steel cathode. The anolyte was the contaminated chromium plating solution and the anode was of lead. The cathode current density was maintained at 10 amperes per square foot. The cell required 5.5 volts potential and .2 ampere were passed continuously through a membrane area of about .785 of a square inch. This gave an equivalent of about .34 ampere per square inch of membrane surface area. The reactions were as follows:

At the anode:



In addition, oxygen was generated on the anode surface.

At the cathode:



In addition, hydrogen was generated on the cathode surface.

The gain of cations in the catholyte is indicated as follows:

- (1) Zn^{2+}
- (2) $\text{Fe}^{3+} + e \rightarrow \text{Fe}^{2+}$
- (3) Ni^{2+}
- (4) Cr^{3+}

After about 25.6 ampere hours of electrodialysis, the catholyte solution was analyzed and it was determined that it had gained in cations as follows:

- (1) Copper as metallic copper=0.42 gram. By arbitrarily assigning $\frac{1}{16}$ of the total power for copper deposition, the efficiency of copper removal was found to be 21.3% of the theoretical.
- (2) Zinc=0.59 gram, found by analysis in catholyte. By arbitrarily assigning $\frac{1}{16}$ of the total power for zinc removal, the efficiency of the zinc removal was found to be 29.7% of the theoretical.
- (3) Iron=0.378 gram, found by analysis in catholyte. By arbitrarily assigning $\frac{1}{16}$ of the total power for iron removal, the efficiency of the iron removal was found to be 15.85% of the theoretical.
- (4) Nickel=0.3696 gram, found by analysis in catholyte. By arbitrarily assigning $\frac{1}{16}$ of the total power for nickel removal, the efficiency of the nickel removal was found to be 20.4% of the theoretical.
- (5) Chromium (Cr^{3+})=8.4 grams, found by analysis in catholyte. By arbitrarily assigning $\frac{3}{4}$ of the total power for chromium removal, the efficiency of the chromium removal was found to be 50.5% of the theoretical.

The analysis of the anolyte after the 25.6 ampere hours of electrodialysis shows the following values.

	G./liter
Hexavalent chromium, Cr^{6+} as CrO_3 -----	298.0
Trivalent chromium, Cr^{3+} as CrO_3 -----	52.0
Total chromium as CrO_3 -----	350.0

It was indicated that oxidation reaction of the trivalent chromium resulted in a gain in hexavalent chromium in grams which represented 58.2% efficiency, on the basis of the total power consumed during the electrolysis for the oxidation on the anode surface. Since the trivalent chromium was more often in contact with the membrane surface area, a greater percentage of trivalent

chromium moved across the membrane, at least initially. As the trivalent chromium concentration dropped in the anolyte, due to the loss to the catholyte, and also due to oxidation into the hexavalent chromium, there was a tendency for an increased consumption of power in the removal of cations present in greater concentration initially.

From the above, it will be apparent that previously wasted chromic acid type solutions can be regenerated through electrodialysis, both by removing dissolved metal ions in the nature of foreign metal ions and by regenerating trivalent chromium on the anode to its desired hexavalent state, in order that it may be again available as oxidizing acid for metal attack or removal. I have also found that where the value of a particular metal warrants, the catholyte which holds the metal removed from the process solution can be used in reclaiming the metal. For example, operating at a usual current density of about 10 amperes per square foot, copper in the catholyte will be deposited as an extremely fine powder. Such powder yields a valuable by-product for metallurgical and other needs. Valuable metals such as cadmium, can be easily recovered by neutralizing the catholyte and precipitating the cadmium or by sulfide precipitation from the acidified catholyte, etc.

To provide a maximum efficiency for the primary metal finishing process and the electrodialysis regenerating process, I prefer to utilize a continuous system that will not remove more of the metal contaminant than is detrimental for the metal finishing process. In this manner, I have been able to maintain a pre-determined metal concentration by removing approximately the same amount of metal in the electrodialysis cell as is produced during the finishing process, while continuously reoxidizing the same amount of trivalent chromium as reduced in the metal finishing process. However, I can also regenerate the process solution in 24 hours at a rate corresponding to the consumption of an eight-hour operational process. By these features, I have been able to limit the size of the installation and to enhance the economical performance of the equipment.

The electrodialysis process is basically an ionic transfer of direct current electrical energy, thus a higher concentration of ions that one wants to remove across the membrane will be a contributing factor in the efficiency achieved. That is, metal removal efficiencies will basically depend on the concentration of the metal ions available for transfer through the membrane and the size of the cations. The smaller or more mobile the cation, the easier it is to move it across the membrane surface. A certain amount of selectivity is noticeable when applying electrodialysis to an electrolyte solution containing a variety of cations or anions. As an example, in a chromium plating solution containing copper, nickel, zinc and iron as impurities and employing a cation permeable membrane, the predominant cations moving through the membrane will be the copper ions. Thus, the copper ions will be depleted before or reduced faster than the zinc, iron or nickel contaminants that will be removed, but at a reduced rate. A condition of 100% current efficiency would be one where all the current applied to the system, that is all the electrons applied to the electrolyte, will be used to transfer or move the cations through the membrane. Actually, hydrogen ions will also be transferred therethrough. This leads to a reduced efficiency against the theoretical 100%. In applying the procedure to a chromic oxide type electrolyte containing copper, I have found, for instance, that the average efficiency in removing the copper from the solution is about 25% of the theoretical.

I have importantly discovered that a good appreciable improvement in efficiency can be accomplished by solution agitation on the membrane surface, in that this assures that cations are always available for the ion exchange material in the membrane to pick-up and release as ions into the catholyte. It is important in carry-

ing out my invention to provide a catholyte with a good solvent action on the metallic ions which it is to receive through the membrane from the process solution being treated or regenerated. It is also important to provide a high enough concentration of cations to be transferred at the membrane surface to improve the efficiency of cation transfer through the membrane relative to the electric current employed. A good working condition is to reduce the contaminants below what would be considered a half-spent bath solution. By way of example, I have employed a chromic acid bright dip for copper of a spent nature that contained about 21 grams per liter of copper. I endeavored to provide for removal of the copper to a level about 1/2 of the indicated content. The procedure showed the following results:

Electrodialysis of chromic acid bright dip for copper

Analysis of used solution (anolyte) 3.8 liters:

	G./liter
Cr ⁶⁺ as CrO ₃ -----	432.5
Cr ³⁺ as CrO ₃ -----	166.5
Total as CrO ₃ -----	598.0
Cu -----	21.0

The used solution was then electrolyzed in a cell with cation permeable membrane catholyte, 10% by volume hydrochloric acid solution, lead anode and stainless steel cathode, cathode current density 10 ASF at 4 volts, and a total of 141 ampere hours used.

Analysis of regenerated solution:

	G./liter
Cr ⁶⁺ as CrO ₃ -----	493.0
Cr ³⁺ as CrO ₃ -----	104.0
Total as CrO ₃ -----	597.0
Cu -----	10.8

At the cathode: $\text{Cu}^{+} + 2\text{e}^{-} \rightarrow \text{Cu}^{\circ}$

Theoretically at 100% efficiency, copper removed = 167.2 g.

Actually, copper removed = 42.56 g.

Actual efficiency = 25.5%

At the anode: $\text{Cr}^{3+} - 3\text{e}^{-} \rightarrow \text{Cr}^{6+}$

Theoretically at 100% efficiency = 91.23 g.

Actually, 32.5 g.

Actual efficiency = 35.7%

The copper removed from the chromic acid solution was collected as an extremely fine metallic powder.

In FIGURES 1 to 5 of the drawings, I have shown an electrodialysis cell unit or apparatus suitable for carrying out my invention. As shown particularly in FIGURES 1, 3 and 5, the apparatus employs an open top container 10 that is carried or supported within an upright stand or support frame 11. The stand 11 may be positioned on a plant floor so as to carry the bottom portion of the container 10 in an upwardly-spaced relation from the floor level. The unit disclosed is of a multi-part or cell type having, as shown particularly in FIGURE 1, vertically or downwardly-projecting, spaced-apart, pairs of compartments or cathode chambers A₁-A₂ and A₃-A₄ that are separated by intermediately-positioned anode compartments or chambers B₁ and B₂. The anode chambers project vertically-downwardly along and between the spaced pairs of cathode chambers. As shown particularly in FIGURE 3, each anode chamber B₁ and B₂ is defined by and separated from an adjacent pair of cathode chambers A₁-A₂ and A₃-A₄ by a pair of vertically-extending spaced-apart permeable ionic membrane members 17.

The container 10 is shown constructed of channel-shaped or flanged plastic or resin side and bottom plate members 12 and 27 and side and bottom plastic or resin plate members 13 that are secured together at their flanges in a spaced-apart insulating relation with respect to each other by through-extending fastening or bolts 14. For uniform reference, I have designated spacing insulation, such as a solution-resistant non-conductive resin material

as *a*. The end chambers A_1 - A_4 are closed-off by front and back transversely-extending plastic or resin plate members 15 and 16 that are secured by the bolts 14 to side members 12 of the respective cathode chambers.

An overflow return trough C for receiving catholyte solution from open top portions of catholyte or cathode chambers A_1 , etc., extends along one outer side of the container 10, adjacent its upper end portion. The catholyte trough C is provided by flanged plastic or resin plate or channel members 19 and 20 that are secured together and to projecting portions of the end plate members 15 and 16 with gaskets *a'* therebetween and by means of bolts 14. A bottom plate member 21 closes-off the bottom of the trough C to form an elongated overflow container for the catholyte solution. A threaded outlet connector 25 extends through the front plate 15 to provide a catholyte fluid-return outlet from the trough C. In a like manner, flanged side plate or channel members 19' and 20', a bottom member 21' and extension portions of the front and back plate members 15 and 16 provide an overflow return trough D along the opposite side of the container for the anolyte solution. The trough D has a threaded outlet connector 26 extending from back plate member 16 to provide a return flow outlet for the anolyte solution.

The catholyte solution enters the trough C, due to a downwardly-offset or cutout upper edge portion 12*a* of each of the plate members 12, along the one side of the container 10. In a like manner, the plate members 13 on the opposite side of the container 10 have downwardly-offset or cutout upper edge portions 13*a* to provide overflow of the anolyte portion into the trough D from the anode or anolyte solution containing chambers B_1 and B_2 .

Adjacent cathode chambers, such as A_2 and A_3 are separated or closed-off with respect to each other by a cross-extending, intermediate plate member 18, see particularly FIGURE 1 of the drawings. For periodic removal of contaminated catholyte solution and sediment from the cathode chambers, the bottom of each of these chambers is provided with a downwardly-sloped central offset bottom portion 27 and a return or outlet flow connector 28. The construction, as shown particularly in FIGURE 1, enables deposited copper or other metal powder to be collected and moved out with the catholyte solution from the bottom portions 27. It will be noted that the bottom portions 27 are also secured in place by bolts 14.

For energizing or supplying electric current to the anode and cathode chambers, pairs of overhead-positioned and supported, longitudinally-extending, positive and negative bus bars are provided, as shown particularly in FIGURE 1. They are connected to a suitable source of direct current. Positive bus bars 30 are positioned at their opposite ends outside of the container 10 by upwardly-projecting channels 33 that are secured to the end plate members 15 and 16 and that form a unitary part of the support frame 11. In a like manner, the negative bus bars 31 are carried and supported by upwardly-projecting channel members 32 that form a unitary part of the support frame 11 and that are secured to the end plate members 15 and 16. As shown, the bus bars 30 and 31 are mounted with respect to the channel members 32 and 33 by insulated bolts 14 and by insulating material *a*, such as hardwood or Micarta resin.

As shown particularly in FIGURES 2 and 3, a metal cathode 35 of a suitable metal, such as of nickel or nickel alloy, is suspended by and electrically-connected to the overhead bus bars 31 by hook-like hangers 36. As shown in FIGURE 2, each hanger 36 has a flat portion or tab portion that is brazed to a cathode member 35 and has an upwardly-projecting twisted or turned portion provided with a hook end to rest on one of the negative bus bars 31. As shown in FIGURE 3, each cathode chamber is provided with a cathode 35 that is suspended in a downward centrally-positioned relation therein. As shown particularly in FIGURES 4 and 5, a metal anode plate mem-

ber 38 of a suitable material, such as of lead or a lead alloy, is suspended from and electrically-connected to the positive bus bars 30 by means of hangers 39. The hangers 39 are secured to the plates 38 and are of similar construction to hangers 36 of FIGURE 2. As shown particularly in FIGURES 3 and 5, I provide an anode plate member 38 for each of the anode chambers which is suspended downwardly-centrally therein in a spaced relation from the side wall and bottom walls thereof.

Catholyte solution is supplied to the cathode cells by means of downwardly-extending inlet or forward flow pipes 40 that project downwardly along the inside of the container 10, along one end of each cathode chamber, and outwardly over the solution trough D. Each cathode chamber is provided with a pipe 40. The pipe 40 at its outwardly-extending portion has a threaded connector 40*a*; its vertical portion 40*b* has an open end 40*c* which terminates in a spaced relation above the bottom of the corresponding cathode chamber.

On the opposite side of the container 10, anolyte supply pipes 41 are provided, one for each of the anolyte chambers. Each pipe 41 has a connector end portion 41*a* which extends horizontally across and above the trough C and has a vertically-downwardly-extending leg portion 41*b* that terminates in a horizontal bottom or foot portion 41*c*. It will be noted that the portions 41*b* and 41*c* extend in a spaced relation between the inside of the container 10 and edges of the anode 38. The bottom or foot portion 41*c* is provided with groups of upwardly-open ports 41*d* through which the anolyte solution is introduced into the corresponding anode chamber or zone part of the container 10.

In FIGURE 6, I have shown a representative system employing my invention and utilizing a suitable electro-dialysis cell unit, such as 10, that has been previously described. A catholyte solution tank or station E is shown adjacent one end of the cell 10, and a metal treating tank F is shown adjacent the other end. Return flow of catholyte from the outflow trough C is accomplished through connector 25 and pipe line 45 to the tank E, and thus serves as a return flow line taking-off solution from the top portion of each of the cathode chambers A_1 , A_2 , A_3 , A_4 , etc. A forward flow of catholyte solution from the tank E is accomplished through pipe line 46, a valve 47, to the inlet or suction or negative pressure end or side of a motor-driven fluid pump 48, and from the outlet or positive pressure side or end of the pump 48, through pipeline 49, valve 50, and pipeline 51, to a header or manifold 52 which is connected to the inlet or forward flow pipes 40 of the cathode chambers. In this manner, a positive, continuous flow or circulation of the catholyte solution may be effected between the container 10 and the solution tank E. This enables an agitation of the catholyte solution in each of the cathode chambers of the multi-part cell along the membrane members 17. Periodically, deposited metal powder-containing catholyte solution may be removed or withdrawn from the bottom portions 27 of the cathode chambers through outflow connectors 28, a header or manifold 29, through pipeline 53, valve 54, the inlet end of the pump 48, the outlet end of the pump 48, pipeline 49, valve 55, filter 56 and pipeline 57 into the tank E.

It will thus be apparent in the normal operation of the system, fluid valves 47 and 50 are open and fluid valves 54 and 55 are closed. However, when catholyte is to be positively withdrawn from the bottom portions of the cathode chambers, valves 47 and 50 are closed, and valves 54 and 55 are opened. In the latter situation, the filter 56 may be used to take out precipitated metal, such as copper, before the catholyte solution is returned through line 47 to the cathode tank E. If the metal content of the catholyte solution is fully dissolved therein, then it may be treated at a station position represented by the filter 56 for precipitating it out, if it is to be recovered or if at

least a portion of it is to be removed to maintain a good working condition of the catholyte in the tank E.

Anolyte solution which is represented by the chromium acid containing treating solution that is to be reconditioned or renewed, is supplied from the tank F. The tank F may be the actual treating tank in which a metal product is being pickled or plated, electrochemically or chemically. The solution positively is moved forward from the tank F through pipeline 60 into the suction or inlet end of a motor-driven fluid pump 61, from the positive pressure or delivery end of the pump 61 through pipeline 62, header or manifold 63 into pipes 41 of the anode chambers B₁ and B₂. Return flow is provided from the anolyte trough D through outlet 26 and pipeline 64 into the tank F. It will thus be apparent that the movement of the anolyte solution may also be accomplished continuously by pumping to agitate the solution in the anode chambers along the extent of the diaphragms 17. Also, the metal treating solution of the tank F may be continuously reconditioned at a rate corresponding to a rate of its contamination by dissolved foreign metals and by the conversion of hexavalent chromium to trivalent chromium. Thus, the treating solution in the tank F may be maintained in a fully usable condition so that the treating operation can be continually accomplished.

I claim:

1. A procedure for reclaiming chromic acid containing electrolytic treating solution that is in a used condition due to the presence of trivalent chromium and of dissolved foreign metals therein which comprises, providing an electro-dialysis cell having an anode compartment containing an anode and a cathode compartment containing a cathode, and also having a cation permeable membrane between the compartments; introducing an acidic catholyte solution into the cathode compartment of the cell and introducing the used condition treating solution as an anolyte solution into the anode compartment of the cell, electrically energizing the cell and moving dissolved foreign metal ions from the anolyte solution through the membrane into the catholyte solution while maintaining the membrane permselective to restrict the passage of chromium ions therethrough from the anolyte solution to the catholyte solution, and also reoxidizing trivalent chromium in the anolyte solution into hexavalent chromium and thereafter removing reconditioned solution from the anode compartment.

2. A procedure as defined in claim 1 wherein a minimum amount of dissolved foreign metal is maintained in the anolyte solution during the reconditioning.

3. A procedure as defined in claim 1 wherein foreign metal transferred to the catholyte solution is recovered from the solution in metallic form.

4. A procedure as defined in claim 1 wherein, the reconditioning of the treating solution as an anolyte is effected in the cell at a rate corresponding to a rate of build-up of foreign metal ions and conversion of hexavalent chromium to trivalent chromium being effected within a chromium acid containing solution as employed in a metal treating operation.

5. A procedure as defined in claim 1 wherein the anolyte solution is positively agitated within the cell along the membrane.

6. A procedure for reconditioning a chromic acid containing metal treating solution that is out of condition due to the presence of trivalent chromium and of dissolved foreign metal therein which comprises, providing an electro-dialysis cell having an anode and a cathode separated by a cationic membrane, introducing an acidic catholyte solution into the cell on the cathode side of the membrane, introducing the metal treating solution to be conditioned as an anolyte solution into the cell on the anode side of the membrane, applying electrical energy to the cathode and anode of the cell and passing dissolved foreign metal ions from the anolyte solution through the

membrane into the catholyte solution while restricting the passage of chromium ions through the membrane to the catholyte solution, and simultaneously with the passing of the foreign metal ions through the membrane, reoxidizing trivalent chromium in the anolyte solution on the anode into hexavalent chromium, and thereafter removing the reconditioned anolyte solution from the cell for reuse as a chromium acid containing metal treating solution.

7. A procedure as defined in claim 6 wherein, the metal treating solution is employed as a solution for conditioning metal in a separate container, portions of the treating solution are progressively circulated between the cell and the container, and the rate of reconditioning of progressive portions of the treating solution as an anolyte solution in the cell is proportioned to the rate of build-up of foreign metal ions and conversion of hexavalent chromium into trivalent chromium that is effected in the separate container.

8. A procedure as defined in claim 6 wherein, the dissolved foreign metal of the anolyte solution is of the class consisting of copper, iron, zinc, nickel and cadmium, and the dissolved ions of different foreign metals in the anolyte solution are selectively passed through the membrane into the catholyte solution.

9. A procedure as defined in claim 6 wherein, the catholyte solution is circulated through the cell, is removed from the cell and filtered, and is then returned to the cell for reuse therein.

10. A procedure as defined in claim 6 wherein, electrically charged foreign metal ions are continuously passed through the membrane to maintain an electric circuit between the cathode and the anode of the cell during the reconditioning of the anolyte solution therein.

11. A procedure as defined in claim 6 wherein the catholyte and anolyte solutions are agitated on the membrane surface during the application of electric current to the cell in such a manner as to maintain an availability of cations for the membrane.

12. A procedure as defined in claim 6 wherein the catholyte solution contains a chemical compound in the nature of hydrochloric acid having a good solvent action on the metallic ions that are passed through and received from the membrane.

13. A procedure for reconditioning a chromic acid containing treating solution for metals that is in a used condition due to the presence of a concentration of trivalent chromium and of dissolved foreign metals which comprises, continuously circulating the used treating solution between a metal treating container and a dialysis cell and utilizing the treating solution as an anolyte solution within the cell, continuously circulating an acidic catholyte solution through the cell that has a good solvent action on the foreign metal ions, separating anode and cathode sides of the cell by a permeable cationic membrane, applying electrical energy to the cell and simultaneously moving dissolved foreign metal ions from the anolyte solution through the membrane into the catholyte solution and reoxidizing trivalent chromium within the anolyte solution into hexavalent chromium.

14. A procedure as defined in claim 13 wherein the reconditioned anolyte solution is removed from the cell and is then reused in a metal treating operation in the nature of an electroplating or pickling operation in which foreign metals are again dissolved therein and hexavalent chromium is again reduced into trivalent chromium.

15. Apparatus for reconditioning a used chromic acid containing metal treating solution that is substantially exhausted due to its content of dissolved foreign metals and of trivalent chromium which comprises, an electro-dialysis cell provided with at least one cathode and one anode, a cationic membrane between the cathode and anode and dividing said cell into the cathode and anode chambers, a catholyte solution tank, a metal treating solution tank, fluid connections between the cathode chamber

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of said cell and said catholyte solution tank, means in said connections for positively moving the catholyte solution between said catholyte solution tank and the cathode chamber of said cell, fluid connections between said metal treating solution tank and the anode chamber of said cell, means in said latter connections for positively moving the metal treating solution between said metal treating solution tank and the anode chamber of said cell to provide an anolyte solution in the anode chamber, and means for supplying electrical energy to said cathode and anode for energizing said cell and moving dissolved foreign metal ions from the anolyte solution in the anode chamber through said membrane into the catholyte solution of the cathode chamber and for simultaneously oxidizing trivalent chromium in the anolyte solution into hexavalent chromium on said anode.

16. Apparatus as defined in claim 15 wherein, said means for circulating the catholyte solution includes a fluid pump, valves and a filter, a fluid return flow connection extends from a bottom portion of the cathode chamber of said cell through one of said valves to a negative pressure side of said pump, and a fluid return flow connection extends from a positive pressure side of said pump through a second of said valves and said filter to said catholyte solution tank for periodically returning contaminated catholyte to said catholyte solution tank; said means for circulating the catholyte solution also includes a fluid return flow connection that extends from a top portion of the cathode chamber to said catholyte solution tank, and a forward fluid flow connection that extends from said catholyte solution tank through a third of said valves to the negative pressure side of said pump and from the positive pressure side of said pump through a fourth of said valves to the cathode chamber of said cell for normally circulating catholyte solution between said catholyte solution tank and the cathode chamber of said cell.

17. Apparatus as defined in claim 16 wherein, said cell has a plurality of cathode and anode chambers, at least one of said anode chambers is positioned between a pair of said cathode chambers, and said pair of cathode chambers are separated from said one anode chamber that is positioned therebetween by a pair of spaced-apart membranes that define said anode chamber.

18. Apparatus for reconditioning a used metal treating solution which comprises, an open-top electro dialysis cell container, spaced-apart pairs of permeable ionic resin membrane members dividing said container into ver-

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tically-extending anode chambers and vertically-extending and spaced-apart pairs of cathode chambers, overhead positive and negative electrical current-carrying bus bars supported above said container, metal cathodes suspended from said negative bus bar and projecting within the cathode chambers, metal anodes suspended from said positive bus bar and projecting within said anode chambers, said pairs of spaced-apart membrane members defining each of the anode chambers and separating them from the cathode chambers, down-flow inlet pipes projecting downwardly along one side of said container into the cathode chambers for supplying a catholyte solution to said cathode chambers, an outlet trough secured to said container along an opposite side thereof and having a downwardly-offset overflow wall portion to pass catholyte solution from upper portions of the cathode chambers into said trough, bottom outlets projecting downwardly from the cathode chambers for removing contaminated catholyte solution therefrom, down-flow pipes projecting downwardly along the opposite side of said container into the anode chambers and along the bottom of said container for supplying the metal treating solution an anolyte solution to the anode chambers, and an outlet trough secured to said container along the one side thereof and having a downwardly-offset overflow wall portion to pass the anolyte solution from upper portions of the anode chambers into said trough.

19. Apparatus as defined in claim 18 wherein, means is provided for positively circulating the anolyte solution through the anode chambers and the catholyte solution through the cathode chambers, and said bus bars supply electrical energy to said cathodes and anodes for reconditioning the anolyte solution contained within the anode chambers.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,481,851 Dated December 2, 1969

Inventor(s) Leslie E. Lancy

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

- Column 2, line 52, change "attach" to --attack--.
- Column 5, line 13, correct the spelling of "molecules";
- line 56, change "by" to --my--.
- Column 14, line 23, change "an", first appearance, to --as--.

SIGNED AND
SEALED
JUN 2 1970

(SEAL)

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