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[54] **CONCENTRATION OF ELECTROLYTE
FROM DILUTE WASHINGS BY
ELECTRODIALYSIS IN A CLOSED
SYSTEM**

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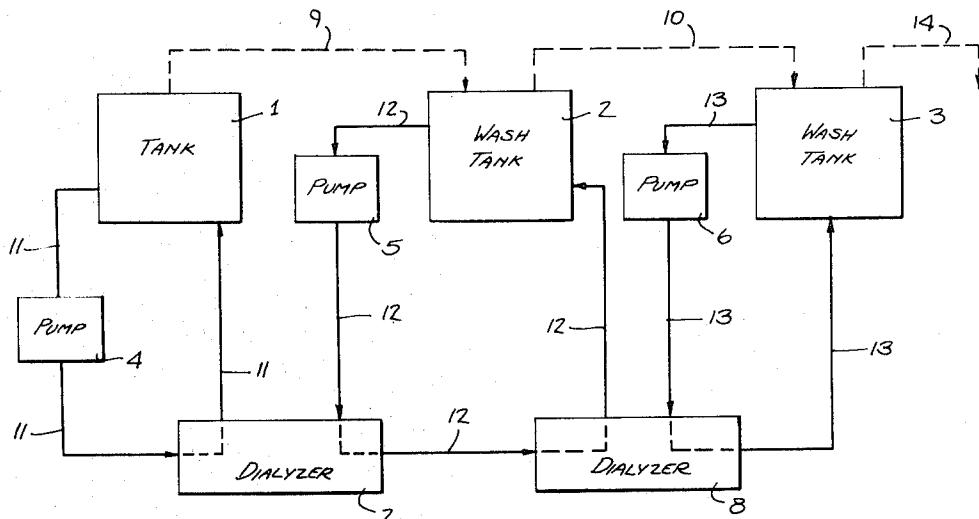
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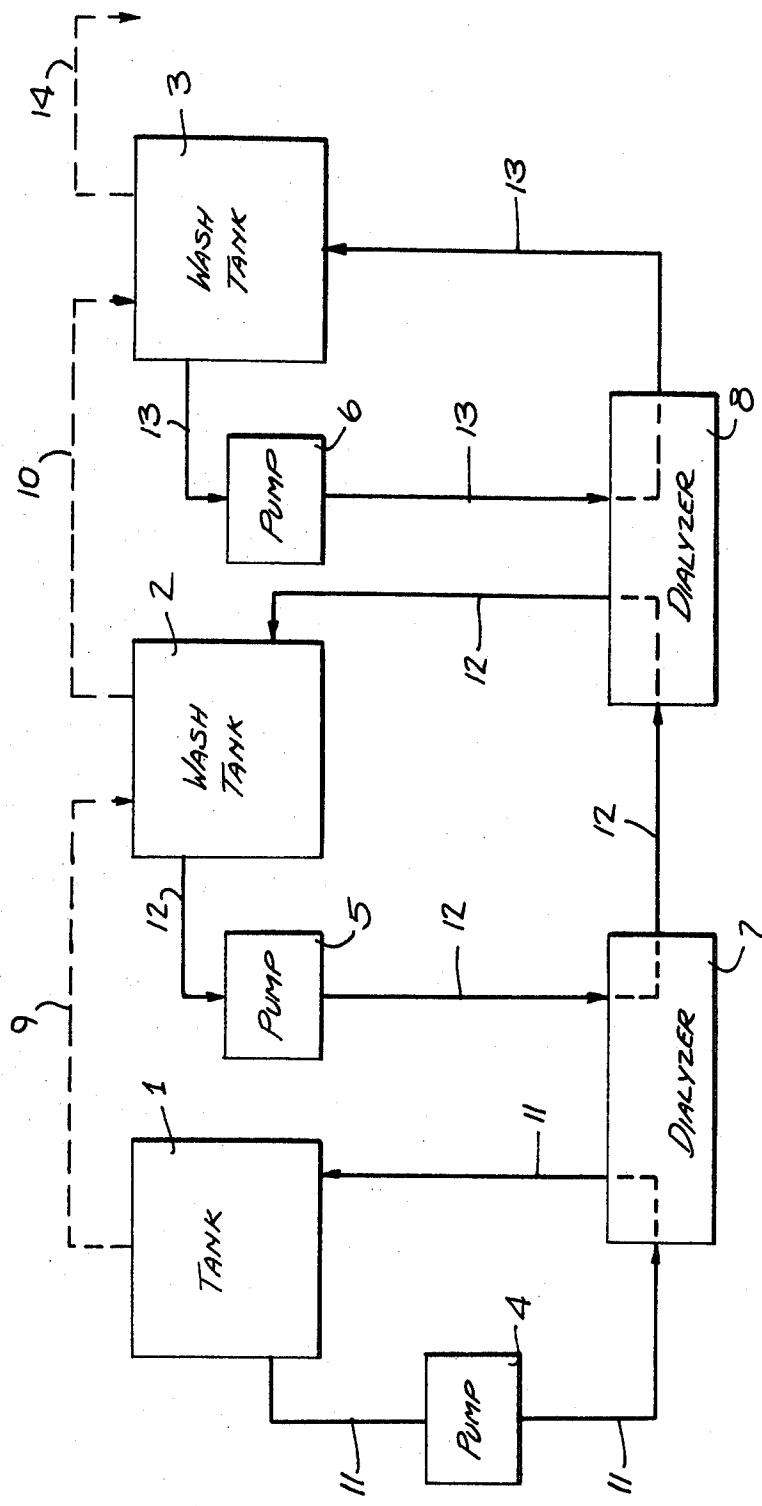
ABSTRACT

Work from electroplating or metal finishing is washed by immersion in a series of solutions. The dragout of electrolyte which remains in the wash solutions is balanced by the transfer of electrolyte from each wash solution to a previous solution of the sequence or to a solution of the original bath concentration. This transfer of electrolyte is by electrodialysis in which a circulating stream of each wash solution acts as a diluting stream in relation to a circulating stream of a previous solution and as a concentrating stream in relation to a subsequent solution.

Extremely high ratios of concentration are achieved between wash stages by operation of the electrodialysis stack under conditions of membrane polarization.

13 Claims, 1 Drawing Figure





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**CONCENTRATION OF ELECTROLYTE FROM DILUTE
WASHINGS BY ELECTRODIALYSIS IN A CLOSED
SYSTEM**

BACKGROUND OF THE INVENTION

In the electroplating and metal finishing industry, metal or metallized plastic which leaves the plating or chemical bath carries some of the solution by surface adhesion. This is called "dragout" and it must be removed by washing with water or with an aqueous solution. If the components of the finishing bath are not removed, the work may be stained or corroded and, in some cases where the components are toxic, they may be hazardous to health, particularly in the case of cyanides and chromates.

The washing may be by a flowing stream of water when the water is plentiful and inexpensive and where the disposal of large volumes of dilute waste solution is not a problem. Increasingly, however, there are limitations to the availability of water of suitable quality and to the volume of waste solution. This is true particularly when the waste must be treated in accordance with requirements of federal, state and municipal authorities and where the cost of treatment is directly related to the volume of the waste.

It is customary to achieve a saving in the volume of waste solution for treatment and in the volume of water for washing by utilizing a sequence of washing steps in each of which the work is immersed in the wash solution and then removed, allowing the solution to drain for a prescribed time. In such a wash system each of the wash solutions is more dilute than the previous one so that the concentration of the solute diminishes in the solution dragout.

The advantage of such a system over the simpler system employing a flowing stream is that most of the dissolved material is removed in the earlier stages at a relatively high level of concentration. Usually it is a practice to add fresh water to the final rinse solution tank. As the volume of this solution increases there is an overflow into the next more concentrated solution tank which, in turn, overflows to the next until from the first wash solution tank the overflow is sent to a waste treatment system and/or to the sewer.

For any given number of washing stages there is a washing efficiency which is defined as the percentage of dissolved material in the work going to the first wash tank which is removed from the work by the system. The greater the amount of wash water and waste the greater is the efficiency. The washing efficiency is greater, or the volume of waste water is less, the greater the number of washing stages. However, beyond three or four stages, the gain is marginal in relation to the increase in capital and operating costs.

For the treatment of the waste effluent solutions there are methods of chemical and biological conversion to eliminate noxious components of the stream or to render them innocuous. Adsorption by activated carbon and by ion exchange resins may accomplish the removal. Economic considerations usually necessitate the regeneration of the adsorbent, always at substantial cost. Electrodialysis is also a method which has been proposed. In this method the electrolyte components of the waste stream are removed and recovered in a more concentrated stream for reuse or disposal.

To illustrate the methods of the prior art for the treatment of plating and metal finishing wastes, we may select as typical, the waste from the plating of copper with cyanide, nickel plating solution waste and the waste solutions from the chrome pickling of brass mill products.

For the treatment of copper cyanide wastes the usual practice is to chlorinate by treatment with calcium hypochlorite. Cyanides are readily oxidized to cyanates which, though far less toxic than the cyanides, are usually oxidized further to produce nitrogen gas and carbon dioxide or carbonates. Oxidation of the cyanates is possible with adequate contact time and pH control. In the combined treatment the copper and cyanide values are lost and the cost of reagent chemicals is considerable. The waste, after treatment, must be held long

enough to be tested to determine that it is innocuous within the cognizant specifications.

Nickel plating solution waste is treated with a lime slurry to a predetermined pH to precipitate calcium sulfate and basic salts of nickel. The solids are removed in a clarifier from which the clear overflow is suitable for reuse while the underflow may be collected in lagoons or it may be removed after dewatering. Very little of the nickel values are recovered.

The dilute waste from the chrome pickling of brass products contains hexavalent chromium, trivalent chromium, copper and zinc sulfates and sulfuric acid. This is treated first with sulfur dioxide or sodium sulfite in an amount which is required stoichiometrically to reduce the hexavalent chromium to trivalent chromium sulfate. Lime is then added to raise the pH to 8-9 to precipitate basic salts of chromium, copper and zinc and calcium sulfate. The water is recovered in the overflow of a clarifier, the underflow going to a lagoon or dewatering filter.

It is obviously advantageous to reconcentrate the components of waste wash solutions without changing them chemically. Electrodialysis is a method which is known to accomplish this concentration by the transfer of the component ions through ion-selective membranes under the driving forces resulting from an electric field.

An electrodialyzer consists of a stack of membranes separated by plastic spacers which enclose cells through which the streams are circulated. The membranes are of two kinds: anionselective and cation-selective, which alternate in the stack. The electric field is induced by electrodes, one at each end of the stack, an anode and a cathode.

The force on the cations is in the direction of the field while that on the anions is in the opposite direction. Those cells which are bounded by membranes such that the field is in the direction from anion-selective to cation-selective are such that the electrolyte is depleted. Where the field is in the direction from cation-selective to anion-selective the solution tends to become more concentrated.

The two types of cells alternate in order in the stack and the solution manifold openings are designed to feed each of the two streams to the appropriate group of cells. One is the concentrating stream and the other is the diluting stream. Usually the two end cells which enclose the electrodes are furnished with electrode rinse streams which are separate from the two principal process streams. These rinse streams are usually recycled.

By these means there is achieved a transfer of electrolyte from the diluting stream to the concentrating stream. Ordinarily the removal of electrolyte, a single electrodialysis stack unit, is limited to from 40 to 50 per cent of that which enters the stack. It is obvious, therefore, that to achieve the very low concentrations which are required in the case of certain waste components it is necessary, in the prior art, to employ numerous stages.

To illustrate: if an effluent stream contains 100 ppm of cyanide, and if it is desired to discharge a stream to waste containing no more than 1 ppm with an electrodialysis system which achieves a 50 per cent reduction in each electrodialysis stack unit it is necessary to employ seven of such units in series. Each of these units requires its own individual pumping system and electrodes.

Many of the plating shops and metal finishing establishments are small in size and hence cannot afford the complexity of such a system and its attendant cost. As a consequence, electrodialysis systems are not used extensively in waste treatment in this industry.

Furthermore, the ratio of demineralization in the methods of the prior art is limited by the membrane transference numbers. To illustrate: if the transference number of the cations in the cation-selective membranes and that of the anions in the anion-selective membranes are both unity there is no limit to the ratio of concentration which can be achieved so long as there is provided an amount of membrane area and electrical

energy which is adequate in relation to the volume of solution and its concentration.

On the other hand, if the transference numbers are less than unity a portion of the current through the cation-selective membrane is carried by anions moving from the concentrated, to the dilute, solution and a portion of the current through the anion-selective membrane is carried by cations moving also from the concentrated, to the dilute, solution. This reverse flow of the ions through each membrane persists even when there is zero current flow and it is then generally ascribed to dialysis, or diffusional transfer of electrolyte from a higher, to a lower, concentration.

Inasmuch as the deficiencies of transference of the counterions in the two types of membranes are additive they impose a limit to the ratio of concentration which can be achieved with the methods of the prior art. Specifically, the transference numbers of electrodialysis membranes fall from unity increasingly as the electrolyte concentration is increased and as the ratio of concentration is increased. The ratio of concentration is therefore, self-limiting.

The deviation of the transference numbers of the membranes from unity is most severe in those systems which include polyvalent ions and especially when these ions are very strongly held by the membranes. When these polyvalent ions are adsorbed by the membrane they not only neutralize the original electric charge of the fixed ionic sites of the membrane polymer but they contribute an excess of the opposite charge. This tends to convert an anion-selective membrane to one which is cation-selective and vice versa.

For example, in the electrodialysis of sodium cuprocyanide solutions, the complex cyanide ions, such as $\text{Cu}(\text{CN})_4^{2-}$, are adsorbed by the anion-selective membranes. These ions are strongly held and tend to neutralize the positively charged quaternary ammonium ions of the polymer and to produce a negative charge which tends to exclude mobile anions and promote the counter movement of sodium ions which carry most of the electric current in the membrane. Although it has been possible to concentrate cuprocyanide solutions by electrodialysis as in U.S. Pat. No. 3,357,823, the current efficiencies are extremely poor when the concentrations are high.

Similar considerations are applicable to the electrodialysis of chromium waste solutions in which the trivalent chromium ion is adsorbed by the cation-selective resin with consequent diminution of the cation transference number and also to the electrodialysis of solutions which contain complex fluorides of iron or aluminum or the polymeric phosphoric acid salts.

It is therefore an object of this invention to provide an improved method and apparatus for washing objects having adhered electrolyte and treating the wash solutions.

A particular object is to maintain the effectiveness of wash solutions by the efficient use of electrodialyzers.

These and other objects of this invention will be apparent from the following detailed description and accompanying drawing.

THE INVENTION

This invention is directed to a method and apparatus for washing adhered electrolyte from a workpiece, in which the efficiency of the wash solutions is maintained by continuously recirculating the wash solutions through a series of electrodialyzers. The workpiece is removed from a treating bath and rinsed in a series of wash baths. The solution from the first wash bath is passed through a first dialyzer which reduces the electrolyte content of the solution by transferring ions to a circulating stream from the treating bath. The solution from the first wash bath is then passed through a second dialyzer which increases the electrolyte content of the solution by taking up ions from a circulating stream from the second wash bath. Extremely high ratios of concentration are achieved between the wash stages by operation of the electrodialyzers under conditions of membrane polarization.

The present invention is further illustrated by reference to the FIGURE which represents schematically a system for the washing of work from a plating or metal finishing operation. This work is removed from tank 1 which contains the plating or finishing solution. It then is immersed successively in wash tanks 2 and 3 with appropriate drainage after leaving each tank. Streams 9, 10 and 14 represent solution which is dragged with the work at each stage. The volume of solution in these three streams is approximately the same but the concentration is lower in each successive stage. Additional stages beyond those illustrated may be used in which each additional stage between tank 2 and tank 3 is constructed and operated in the manner set forth below for tank 2. Tank 1 may also represent a tank from which electrolyte is eventually recovered in accordance with known methods.

Pumps 4, 5 and 6 circulate streams 11, 12 and 13 out of, and back to the tanks 1, 2 and 3. Stream 11 is the concentrating stream passed through dialyzer stack 7. Stream 12 is the diluting stream passed through dialyzer stack 7 and also the concentrating stream passed through electrodialyzer stack 8. Stream 13 is the diluting stream passed through stack 8. Alternatively stream 12 may be passed through dialyzer 7 and then back into tank 2, and a separate stream from tank 2 may be passed through dialyzer 8 and then back to tank 2. However, for efficiency of operation the embodiment of the Figure as illustrated is preferred.

It is thus preferable, though not essential, to mount the electrodialyzer stacks 7 and 8 on a single frame and to provide manifold connections for the flow of stream 12 from the one to the other. Stream 12 flows in parallel relation with stream 11 through dialyzer 7 and similarly streams 12 and 13 flow in parallel relation through dialyzer 8. The design of the electrodialyzer separators, electrodes, end compression heads and manifold connections are those which are well known and the membranes are those which are used in commercial electrolysis in the prior art. Note, for example, the construction and operation of such units as set forth in Diffusion and Membrane Technology, Reinhold Publishing Company, 1962.

Inasmuch as the three streams 11, 12 and 13 are recycled it is not advantageous to provide a very high percentage of electrolyte depletion, or concentration, per pass. It is essential, however, to minimize internal leakage, especially of the concentrating stream into the diluting stream of either stack. This is because of the very high ratio of concentration which can be achieved only in a system with minimum leakage.

The frames and separators of the electrodialyzer stacks should be of non-conductive plastic construction appropriate to the operating temperature. The electrodes should be of a conductive materials, such as metal or graphite, appropriate to the solutions. For cyanide copper solutions the anode may be of stainless steel or an expendable anode of copper. The cathode may be of stainless steel or graphite. For acid chromate solutions the anode may be of lead and the cathode may be of stainless steel. For chloride nickel plating solutions the anode may be of platinized titanium or expendable nickel. The cathode may be of graphite or of nickel. Selection of suitable materials of construction is in all cases in accordance with principles and practice which are well known.

In the use of the present invention with expendable anodes or where there is a metallic deposit on the cathode, the anodes and cathodes are removed and replaced by methods well known to those skilled in the art. Optionally within the scope of this invention electrode wash streams may be utilized to isolate the electrodes from the two principal streams.

Whereas the constructional features of the individual cells, including the membranes, frames and separators are, in accordance with this invention, the same as in the prior art the operation of the process differs in an important respect from that of the prior art. Specifically the stacks are operated, in accordance with this invention, under conditions of concentration polarization at the interfaces of the membranes with the diluting stream.

In the methods of the prior art the electrodialysis system is operated to avoid the concentration polarization which is an essential element of the present invention in its preferred embodiment. The reason for avoidance of concentration polarization in the prior art is to avoid the use of excessive power but more important to avoid pH changes which lead to scale formation particularly on the anion selective membranes. Wash solutions used in the present invention are not subject to scale formation in the operation of the electrodialysis stacks under polarizing conditions.

It is well known that for a given electrodialysis system there is a limiting current density above which concentration polarization occurs and that this limiting current is directly proportional to the electrolyte concentration in the diluting stream. This limiting current density divided by the electrolyte concentration is a linear function of the coefficient of mass transfer at the membrane-solution interface. This is, in turn, a function of a solution flow velocity and the configuration of the flow channel.

It is a purpose of the present invention to operate with a transference number of the counterions in both anion-, and cation-, selective membranes very nearly unity. This is achieved by operation under conditions of concentration polarization of the membranes. Under such conditions of polarization the ion concentration is nearly zero in the diluting stream solution at the membrane interface. Under such operating conditions the concentration of co-ions in the membrane is exceedingly low and the transference number of counter-ions is accordingly very nearly unity.

It has been discovered that if, in the system shown, the tanks 2 and 3 are filled with nearly pure water at the start-up when power is applied to the electrodes of stacks 7 and 8 and when the pumps 4, 5 and 6 are started to circulate the streams 11, 12 and 13, it is relatively easy to maintain a condition of membrane polarization while the concentrations in tanks 2 and 3 are increasing. As the operation of the dragout, 9 and 10, brings electrolyte from the tank 1 to the wash tanks 2 and 3 the current in each stack rises substantially in accordance with the faraday equivalence of the electrolyte in the dragout. This is maintained as long as the voltage between each pair of electrodialyzer stack electrodes is sufficiently high to maintain the condition of membrane polarization.

If the potential is less than that required to maintain the polarizing current the membranes may pass into a condition of lower counter-ion transference number. This leads to a lower current efficiency and consequently, a rise in concentration in the wash tanks, especially in tank 2, as the dragout continues. The increase in concentration in the wash solution leads to further deterioration in membrane transference number and the effect is cumulative leading to a much lower concentration ratio.

The higher the concentration in tank 1 and the greater the dragout in relation to the effective membrane area the greater is the necessity for maintaining membrane performance as measured by the concentration ratio. This is true especially of complex cyanide solutions which have a tendency to "poison" the anion-selective membranes by absorption resulting in a lower anion transference number and lower transport efficiency.

As is well known a condition of membrane polarization in electrodialysis is indicated by a more or less sharp increase in the apparent resistance defined as the rate of increase of voltage with current per cell pair. The increase in apparent resistance is not always sharp because the solution flow and electrolyte concentration are not always uniform over the membrane surface. It has been discovered that in its application to the present invention, membrane polarization is most effective in enhancement of membrane performance when the rate of increase of voltage with current is greater than twice the resistance, i.e., when

$$\frac{dV}{dI} > 2 \frac{V}{I}$$

where I is the current in the stack and V is the stack voltage. This condition may be readily determined by measuring the voltages and currents in the system.

The application of this invention to the recovery of cyanide and copper values from a system for washing copper plated parts is illustrated by the following examples.

EXAMPLES

10 In a system illustrated the electrodialysis stacks 7 and 8 consist of Aquachem Model WD 6-2 electrodialyzers made by Aqua-Chem, Inc., Waukesha, Wisconsin, with nine cation-selective membranes, Ionac MC 3470, and eight anion-selective membranes, Ionac MA 3475 each made by Ionac, Div. of 15 Ritter Pfaulder, Birmingham, N.J. The concentrating stream flowed through the cathode compartment and through alternate cells while the diluting stream flowed through the remaining cells and the anode compartment. The effective area of each membrane was 750 sq. cm and the flow rates 20 were 225 gallons per hour for all streams.

The solution in tank 1 was initially made up with 8 oz/gall of copper cyanide, 9 oz/gall of sodium cyanide, 2.0 oz/gall of soda ash and 4.0 oz/gall of caustic soda. With a voltage of 50 25 volts for stack 7 and 30 volts for stack 8 the ratios of concentration in tanks 2 and 3 to that in tank 1 were as follows for varying rates of dragout.

TABLE I

30	Dragout Rate Liters per hour	Concentration Ratios All Ions Compared	
		Tank 2:Tank 1	Tank 3:Tank 1
35	0.90	1:402	1:106,530
	2.59	1:140	1: 12,040
	3.27	1:129	1: 10,320

The operation of the electrodialyzers at a voltage above membrane polarization is used to effectively provide a ratio of 40 electrolyte concentration of each stage in relation to a previous stage of at least 1:20 and preferably about 1:100. The ratio of course may vary depending on the dragout rate and the electrolyte concentration in the dragout. If the dragout rate increases sharply the concentration ratio may be only 1:5, but as 45 the dragout rate falls off the concentration ratio will increase as the wash streams are continuously recycled through the dialyzer.

Although this invention is employed advantageously using 50 two stages of washing and electrodialysis, it is not necessarily limited thereto. The number of stages and the stack voltages and other parameters may be varied without departing from the scope of this invention. Selection of the operating parameters is determined by the ratio of concentration which is required and by considerations of power and equipment cost.

55 This invention may be applied advantageously to the recovery of the components, including nickel chloride and nickel sulfate, of solutions dragged out of nickel plating baths; of copper sulfate and fluoborate from copper plating baths. It may be applied also to the recovery of complex fluorides of iron and chromium from the dragout of stainless steel pickle 60 solutions and also to the recovery of gold, silver, and zinc values from cyanide bath dragout.

This invention has been described in terms of specific 65 embodiments set forth in detail. Alternative embodiments will be apparent to those skilled in the art in view of this disclosure, and accordingly such modifications are to be contemplated within the spirit of the invention as disclosed and claimed herein.

70 I claim:

1. In the method of treating electrolyte from a solution on solids, wherein the solids are removed from a treating bath and passed sequentially through at least a first and second wash bath containing an aqueous solution, 75 the improvement which comprises,

pumping the solution from said treating bath through the concentration compartments of a first electrodialyzer and returning said solution to said treating bath,
pumping the aqueous solution from said first wash bath through the dilution compartments of said first dialyzer and through the concentration compartments of a second dialyzer and returning said aqueous solution to said first wash bath, and

5 pumping aqueous solution from said second wash bath through the dilution compartments of said second dialyzer and returning said aqueous solution to said second wash bath.

10 2. The method according to claim 1 in which the electrolyte includes one or more complex cyanides of copper, zinc, gold, silver or cadmium.

15 3. The method according to claim 1 in which the electrolyte includes alkaline chromate solutions.

4. The method according to claim 1 in which the electrolyte includes acid chromates and trivalent chromium.

20 5. The method according to claim 1 in which the electrolyte includes nickel sulfate or nickel chloride.

6. The method according to claim 1 in which the electrolyte contains copper sulfate or copper fluoborate.

25 7. The method according to claim 1 in which the electrolyte contains complex fluorides of iron, chromium, or aluminum.

8. The method of claim 1 wherein a series of said solids are passed through said wash baths, and the concentration ratio of electrolyte in said treating bath with relation to said first wash bath is maintained at least at 5:1 and the concentration ratio of electrolyte in said first wash bath in relation to said second wash bath is maintained at least at 5:1.

30 9. A method of continuously recovering electrolyte from a metal finishing bath dragout on solids which comprises sequentially immersing said solids into and removing them from each of a series of vessels comprising a treating vessel and at least two wash vessels wherein each of said vessels contain an aqueous solution more concentrated in electrolyte than the aqueous solution in a subsequent vessel to which solids are transferred, continuously recycling a less concentrated solution from a first one of said vessels between said vessel and the diluting stream cells of an electrodialyzer, continuously recycling a more concentrated solution from a second vessel through the concentrating stream cells of said electrodialyzer, and operating said electrodialyzer to balance 45 the electrolyte removed from the solids in said second vessel by the transfer of electrolyte to said first vessel to maintain the ratio of electrolyte between said vessels at a ratio of at least 5:1.

40 10. The method according to claim 9 in which the electrolyte includes one or more complex cyanides of copper,

zinc, gold, silver or cadmium.

11. In the method of treating electrolyte from a solution on solids, wherein the solids are removed from a treating bath and passed sequentially through at least a first and second wash bath containing an aqueous solution,

the improvement which comprises,

pumping the solution from said treating bath through the concentration compartments of a first electrodialyzer,

pumping the aqueous solution from said first wash bath through the dilution compartments of said first dialyzer and through the concentration compartments of a second dialyzer and returning said aqueous solution to said first wash bath, and

pumping aqueous solution from said second wash bath through the dilution compartments of said second dialyzer and returning said aqueous solution to said second wash bath.

15 12. In the method of treating electrolyte from a solution on solids, wherein the solids are removed from a treating bath and passed sequentially through at least a first and second wash bath containing an aqueous solution,

the improvement which comprises,

pumping the solution from said treating bath through the concentration compartments of a first electrodialyzer,

pumping aqueous solution from said first wash bath through the dilution compartments of said first dialyzer and returning said aqueous solution to said first wash bath, pumping an aqueous solution from said first wash bath through the concentration compartments of a second dialyzer and returning said aqueous solution to said first wash bath, and

pumping aqueous solution from said second wash bath through the dilution compartments of said second dialyzer and returning said aqueous solution to said second wash bath.

20 13. In the method of treating electrolyte from a solution on solids, wherein the solids are passed sequentially through at least a first and second wash bath containing an aqueous solution,

the improvement which comprises,

pumping a solution through the concentration compartments of a first electrodialyzer,

pumping the aqueous solution from said first wash bath through the dilution compartments of said first dialyzer and through the concentration compartments of a second dialyzer and returning said aqueous solution to said first wash bath, and pumping aqueous solution from said second wash bath through the dilution compartments of said second dialyzer and returning said aqueous solution to said second wash bath.

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