

[54] PURIFICATION OF CHROMIUM PLATING SOLUTIONS BY ELECTRODIALYSIS

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[58] Field of Search 204/151, 180 P, 130, 97

[56] References Cited

UNITED STATES PATENTS

3,394,068	7/1968	Calmon et al.	204/180 P
3,423,300	1/1969	Joo et al.	204/97 X
3,481,851	12/1969	Lancy	204/97 X
3,682,796	8/1972	DevBedi et al.	204/97
3,761,369	9/1973	Tirrell	204/151

Primary Examiner—John H. Mack

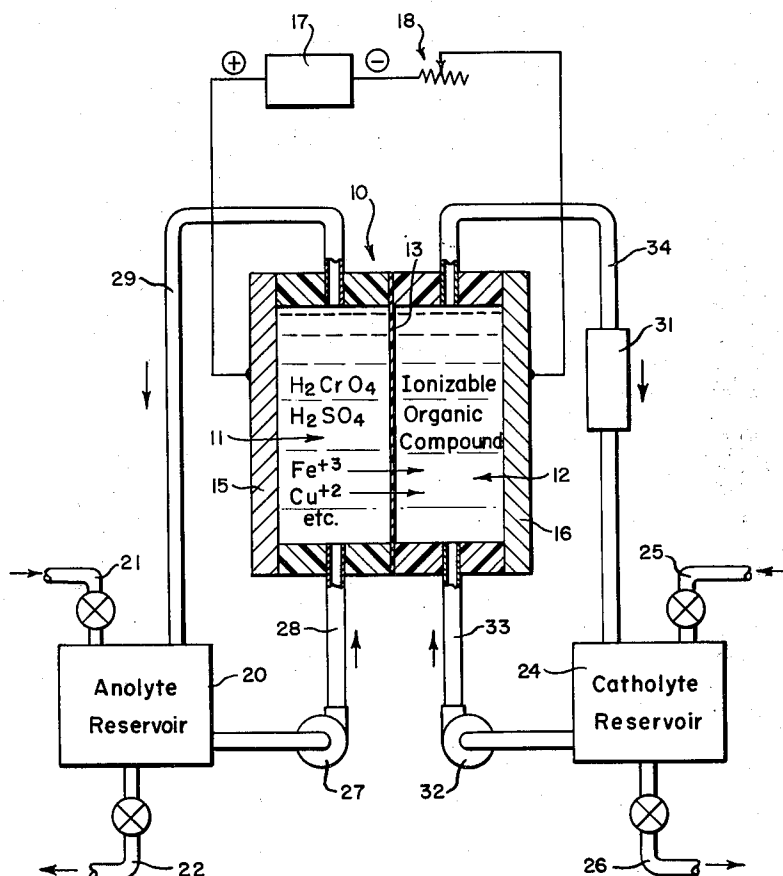
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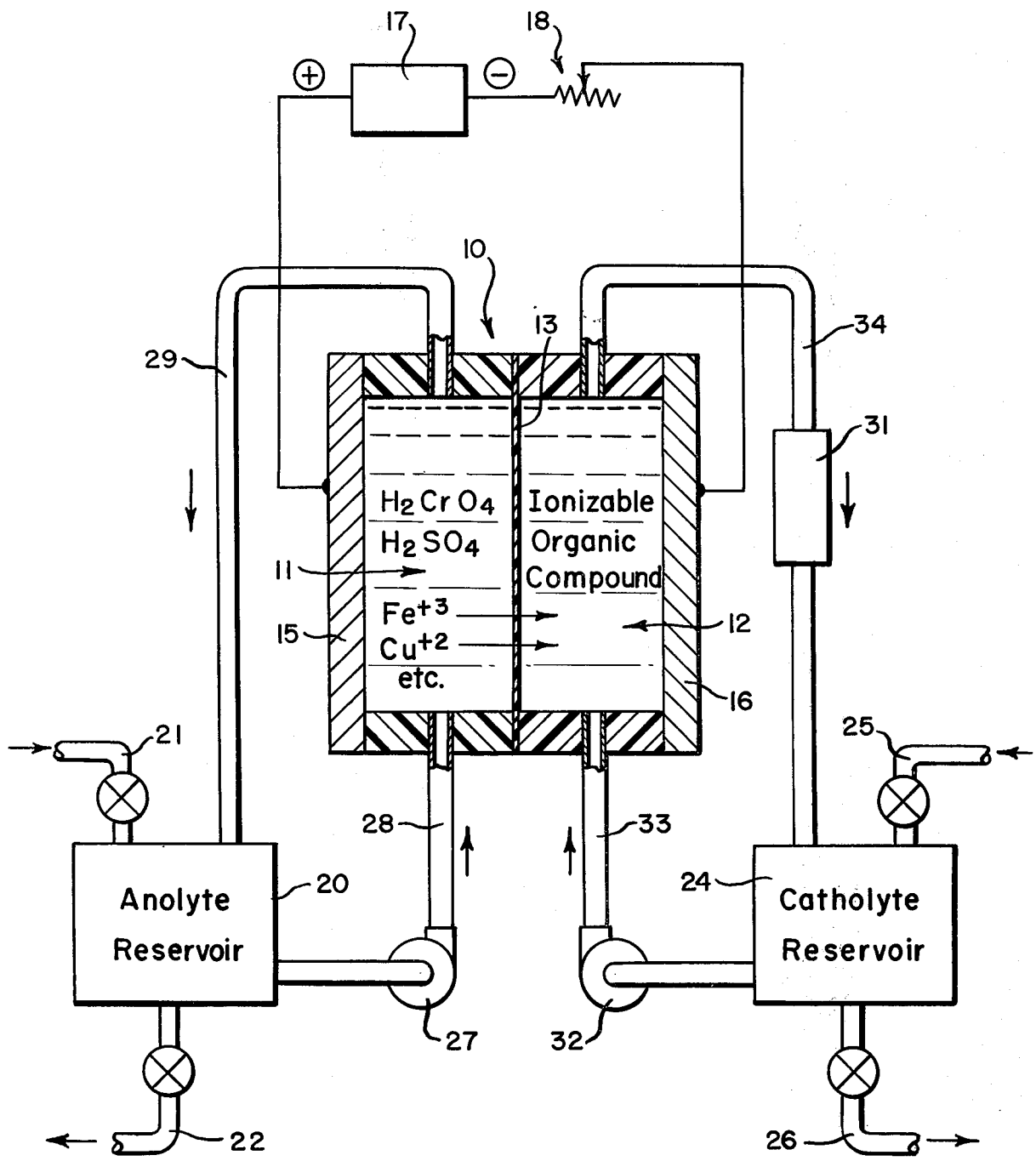
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[57] ABSTRACT

Aqueous solutions of chromic acid containing metallic contaminants dissolved therein are purified by electrodialysis of the solution in a cell having an anolyte compartment containing an anode and a catholyte compartment containing a cathode, the anolyte and catholyte compartments being separated by a cation permeable membrane. The chromic acid solution is contained in the anolyte compartment and comprises the anolyte of the process, and an aqueous solution of at least one ionizable organic compound is contained in the catholyte compartment and comprises the catholyte of the process. An electric current is passed between the anode and the cathode through the anolyte and catholyte to cause contaminating metal cations to migrate from the anolyte through the cation permeable membrane into the catholyte. The anions of the ionizable organic compounds are oxidized to gaseous oxidation products and water when reacted with the chromic acid-containing anolyte, the solubility of said ionizable organic compounds is such that the total concentration thereof in the catholyte is at least 1 Normal, and the dissociation of said organic compounds is such that the conductivity of the catholyte is at least 1.0×10^{-4} mho/cm.

11 Claims, 1 Drawing Figure





PURIFICATION OF CHROMIUM PLATING SOLUTIONS BY ELECTRODIALYSIS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the purification of chromium plating solutions by electrodialysis.

2. Prior Art

Metallic chromium is commonly electroplated onto the surface of a substrate metal to produce a decorative layer of "bright" chromium metal or a wear resistant layer of "hard" chromium metal on the substrate metal. The chromium plating process is subject to a variety of technical difficulties which require close control over the conditions under which the process is carried out in order to obtain acceptable chromium deposits. Among the most important and potentially harmful of these operating conditions is the composition of the chromium-containing electroplating solution and the level of contaminating metals present in this solution.

Chromium plating solutions comprise essentially an aqueous solution of chromic acid (conventionally expressed as chromium trioxide, CrO_3) together with a small amount of sulfuric acid (H_2SO_4) present as a catalyst. The ratio of chromic acid to sulfuric acid ($\text{CrO}_3/\text{H}_2\text{SO}_4$) is usually about 100:1 and plating becomes impossible if this ratio falls below about 40:1 or exceeds about 200:1. The presence of anions other than chromiferous ions and a limited amount of sulfate ions in the chromium plating solution, and in particular chloride, nitrate and phosphate ions, have an undesirable coadjutant catalytic effect and at very low levels will cause unsatisfactory chromium deposits. In addition, the presence of metal cations other than chromium in the chromium plating solution, and in particular copper, iron, nickel and zinc ions, will also cause unsatisfactory results in the electroplating process even when present in very low concentrations. Another factor which can adversely affect the electroplating process is the gradual increase in the ratio of trivalent to hexavalent chromium in the electroplating solution which can occur under certain electroplating conditions.

Trivalent chromium and iron reduce the conductivity of the plating solution and interfere with the throwing power and bright plating of the process. Zinc, nickel and copper tend to produce a haze on the plated surface, and also reduce the throwing power of the solution. The build-up of these metal impurities in the solution is due to the solvent action of the highly corrosive chromic acid solution on copper, zinc, and iron objects that are being electroplated or are otherwise exposed to the plating solution, and to the drag-in of nickel sulfate solution from a previous nickel plating step in the process. When the level of metal contaminants in the solution exceeds acceptable limits the electroplating solution must either be discarded or the contaminant metals in the solution must somehow be removed from the solution.

It has heretofore been proposed by Leslie E. Lancy in U.S. Pat. No. 3,481,851 that the dissolved metallic contaminants be removed from the aqueous chromium plating solution by electrodialysis. Electrodialysis may be defined as the transport of ions through an ion permeable membrane as a result of an electrical driving force, and the process is commonly carried out in an electrodialysis cell having an anolyte compartment and

a catholyte compartment separated by a permselective membrane. In the Lancy process for the purification of chromium plating solutions the chromic acid solution is contained in the anolyte compartment and comprises the anolyte of the cell, and an aqueous solution of a mineral acid (for example, hydrochloric acid) is contained in the catholyte compartment and comprises the catholyte of the cell, the catholyte and the anolyte being separated by a cation permeable membrane.

An electric current is passed between the anode and the cathode of the Lancy cell through the aqueous solutions contained in the anolyte and catholyte compartments of the cell. The electric current causes the contaminant metal cations (for example, iron and copper ions) present in the chromic acid solution to migrate from the anolyte compartment through the cation permeable membrane into the catholyte compartment, reverse migration of anions (for example, chloride ions) from the catholyte compartment into the anolyte compartment being prevented, in theory at least, by the cation permeable membrane. The Lancy process effectively reduces the concentration of contaminant metal cations in the chromic acid solution to acceptable levels. In addition, the electrolytic oxidizing conditions prevailing in the anolyte at the anode quickly oxidizes the trivalent chromium present therein to the hexavalent state, thereby reducing the ratio of trivalent to hexavalent chromium to an acceptable level.

The permselective membrane employed in the Lancy process (and in all similar electrodialysis processes) are not unlike ion exchange resins in sheet or membrane form. They comprise a matrix of a chemically inert resin throughout the polymer lattice of which are distributed chemically bound anionic or cationic moieties having fixed negative and positive charges. Anion permeable membranes have positive (cationic) fixed charges distributed throughout the polymer lattice and, as the name implies, are permeable to negatively charged ions and are relatively impermeable to positively charged ions. Similarly, cation permeable membranes have negative (anionic) fixed charges distributed throughout the polymer lattice and are permeable to positively charged ions and are relatively impermeable to negatively charged ions. Unfortunately, there are no known anion permeable membranes that are 100% impermeable to cations, and there are no known cation permeable membranes that are 100% impermeable to anions. As a result, there is always in every electrodialysis process, including the Lancy process, some small degree of reverse migration of cations through the anion permeable membrane and/or of anions through the cation permeable membrane.

As noted, the Lancy process employs a cation permeable membrane between the anolyte and the catholyte compartments which permits relatively free transfer or migration of contaminant metal cations from the chromium plating solution in the anolyte compartment to the mineral acid-containing solution in the cathode compartment. However, the cation permeable membrane also permits the reverse migration of a small amount of mineral acid anions from the catholyte to the anolyte compartment, and as a consequence there is a fairly rapid build-up of these anions in the chromium plating solution. The build-up of mineral acid anions in the anolyte quickly renders the chromic acid solution unsuitable for chromium plating for the reasons hereinbefore discussed. Therefore, while the Lancy

process will effectively remove harmful metal cations (for example, iron and copper ions) from the chromium plating solution, it also results in the rapid build-up of equally harmful mineral acid anions (for example chloride ions) in the plating solution. As a result, the Lancy process does not provide a satisfactory solution to the problem of rejuvenating chromium plating solutions by the removal of contaminant metal cations therefrom.

After an intensive investigation of the many difficult problems encountered in the rejuvenation of chromium plating solutions by electrodialysis, and in particular the special problems encountered in the Lancy process described above, I have now discovered that contaminant metal cations can be effectively and efficiently removed from these plating solutions without concomitant build-up of harmful anions in the plating solutions provided the composition of the catholyte employed in the process conforms to certain critical criteria that I have established as a result of my investigations. Specifically, I have discovered that if certain water soluble and ionizable organic compounds are employed as the electrolyte material in the catholyte of the process consistently good results are obtained with regard to both the reduction of cationic contamination and the avoidance of anionic contamination of the chromium plating solution. In general, the anions of the dissociated organic compounds must be capable of being oxidized by chromic acid to gaseous oxidation products and water, the solubility of these ionizable organic compounds in water must be such that the total concentration thereof in the catholyte is at least 1 Normal, and the ionic dissociation of these organic compounds must be such that the conductivity of the catholyte is at least about 1.0×10^{-4} mho/cm. In addition, the catholyte advantageously contains a chelating agent for the contaminant metal ions transported there to from the anolyte.

SUMMARY OF THE INVENTION

The process of the invention relates to the removal of dissolved metallic cation contaminants from aqueous solutions of chromic acid by electrodialysis in an electrodialysis cell, and in particular to the purification of contaminated chromium plating solutions. The electrodialysis cell in which the process is carried out has at least one anolyte compartment containing an anode and at least one catholyte compartment containing a cathode, each of the anolyte and catholyte compartments being separated from each other by a cation permeable membrane. The chromic acid solution is contained in the anolyte compartment and comprises the anolyte of the cell, and an anion-containing aqueous solution is contained in the catholyte compartment and comprises the catholyte of said cell. An electric current is passed between the anode and the cathode through the anolyte and the catholyte to cause contaminating metal cations to migrate from the anolyte through the cation permeable membrane into the catholyte. My improvement in this electrodialysis process comprises employing as the catholyte an aqueous solution containing at least one water soluble ionizable organic compound the anion of which must be capable of being oxidized by chromic acid to gaseous oxidation products and water. The solubility of the ionizable organic compounds in water is such that the total concentration thereof in the catholyte is at least 1 Normal, and the ionic dissociation of said organic compounds is such that the con-

ductivity of the catholyte is at least 1.0×10^{-4} mho/cm. The catholyte advantageously contains a chelating agent for the contaminant metal ions transferred thereto from the anolyte. The ionizable organic compounds serve as the electrolyte material in the catholyte and may also serve as the chelating agent therein. Alternatively, a separate chelating agent for the contaminant metal cations may be present in the catholyte.

When the electrodialysis of chromium plating solutions contaminated with such metal cations as iron and copper ions is carried out in conjunction with organic anion-containing catholyte solutions having the characteristics described above, the concentrations of the contaminant metal cations in the anolyte will quickly be reduced to acceptable levels by transfer of these cations through the cation permeable membrane into the catholyte solution. The metal cations thus transferred to the catholyte advantageously form water soluble complexes with the chelating agent present in the catholyte and are thereby largely prevented from precipitating from the solution. In addition, any of the organic anion constituents of the catholyte which may be transported through the cation permeable membrane into the anolyte immediately react with chromic acid contained in the anolyte and are converted to gaseous oxidation products (for example, carbon dioxide) and water. The build-up of organic anions in the anolyte is thereby prevented, and the build-up of mineral acid anions harmful to the chromium plating process is avoided altogether. Other important advantages and features of my improved process for removing contaminant metal cations from chromium plating solutions will be apparent from the following detailed description thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

The improved electrodialysis process of the invention will be better understood from the following description thereof in conjunction with the accompanying drawing which shows, in schematic form, an electrodialysis cell adapted to carry out the process.

DETAILED DESCRIPTION OF THE INVENTION

As shown schematically in the drawing, the electrodialysis process of the invention is carried out in an electrodialysis cell 10 having an anolyte compartment 11 and a catholyte compartment 12 separated by a cation permeable membrane 13. The anolyte contained in the anolyte compartment 11 comprises the chromium plating solution being purified, and the catholyte contained in the catholyte compartment 12 comprises the ionizable organic electrolyte-containing solution of the invention. An anode 15 is disposed so that it is in contact with the anolyte contained in the anolyte compartment 11, and a cathode 16 is disposed so that it is in contact with the catholyte contained in the catholyte compartment 12. The anode 15 and the cathode 16 may be positioned within the anolyte and catholyte compartments, or they may form the outer walls of the anolyte and catholyte compartments, respectively, as shown in the drawing. The anode 15 and the cathode 16 are electrically connected to a source of direct current 17 (advantageously a rectifier), the amount of electrodialysis current being controlled by the current control means 18. The electrodialysis may be carried out in a single cell comprising but one pair of anolyte and catholyte compartments as shown in the drawing, or it may be

carried out in a plurality of pairs of anolyte and catholyte compartments arranged in a stack or bank of cells in the manner known in the art.

As noted, the anolyte comprises the chromium plating solution being purified and the catholyte comprises the ionizable organic electrolyte-containing solution of the invention. Chromium plating solution containing contaminant metal cations from the chromium plating process is continuously delivered to the anolyte reservoir 20 through the conduit 21, and purified chromium plating solution is continuously returned to the chromium plating process through the conduit 22. Fresh organic electrolyte-containing solution is introduced whenever required into the catholyte reservoir 24 through the conduit 25, and catholyte solution is occasionally withdrawn from the catholyte reservoir through the conduit 26 for rejuvenation. Chromic acid-containing anolyte solution from the anolyte reservoir 20 is continuously circulated through the anolyte compartment 11 by means of the pump 27 and the associated tubing 28 and 29, and organic electrolyte-containing catholyte solution from the catholyte reservoir 24 is continuously circulated through the catholyte compartment 12 and the filter 31 by means of the pump 32 and the associated tubing 33 and 34.

The passage of an electric current between the anode 15 and the cathode 16 causes contaminant metal cations in the anolyte to migrate from the anolyte through the cation permeable membrane 13 into the catholyte, reverse migration of organic anions from the catholyte through the cation permeable membrane into the anolyte having no harmful effect on the composition of the chromium plating solution for the reasons herein set forth. The continuous introduction of contaminated chromium plating solution from the chromium plating process into the anolyte reservoir 20, the continuous circulation of the chromium plating solution through the anolyte compartment 11 of the cell 10 with the concomitant continuous transfer of contaminant metal cations from the anolyte to the catholyte of the cell, and the continuous withdrawal of purified chromium plating solution from the anolyte reservoir 20 for return to the chromium plating process, results in the maintenance of the metal cation contamination of the plating solution at very low levels and permits the concentration of chromic acid in the plating solution to be maintained at optimum levels (for example, from 10 to 15% chromic acid.)

The electrodialysis cell 10, the anolyte and catholyte reservoirs 20 and 24, and the pumps, filters and tubing associated therewith must be constructed from materials that are inert with respect to the anolyte and catholyte solutions, and in particular to the chromic acid-containing anolyte solution. The anode 15 and the cathode 16 are advantageously made of stainless steel, and the non-conductive parts of the cell (apart from the cation permeable membrane 13) and the tubing associated therewith are advantageously made of such chemically inert plastic materials as polyethylene, polypropylene and polyfluorochloroethylene. The cation permeable membrane 13 comprises a thin sheet of film of a chemically inert resin throughout the polymer lattice of which are distributed chemically bound anionic moieties having a fixed negative charge. In addition to its cation permeable properties, the membrane 13 should be strongly hydrophilic; it should be a reasonably good electrical conductor and should have ade-

quate physical strength when immersed in aqueous electrolyte solutions, and it should be resistant to attack by the chromic acid-containing anolyte solution. There are a number of such cation permeable membranes available from commercial suppliers, and I presently prefer to use a perfluorosulfonic acid membrane manufactured by DuPont and sold under the name "Nafion".

The chromium plating solution employed as the anolyte in the process comprises, typically, an aqueous solution of chromic acid and sulfuric acid contaminated with a minor amount of dissolved iron, copper and other foreign metals, the ratio of chromic acid to sulfuric acid in the solution being between about 40:1 to 200:1. If, as suggested in U.S. Pat. No. 3,481,851 to Lancy, hydrochloric acid is employed as the electrolyte in the catholyte, chloride ions are transferred from the catholyte to the anolyte by reverse migration through the cation selective membrane, and as a result the chromium plating solution rapidly becomes unuseable due to chloride contamination. Similar results are experienced when other mineral acids such as nitric acid and phosphoric acid are employed in the catholyte. Sulfuric acid is an essential constituent of chromium plating solutions, and a moderate limited build-up of sulfate ions in the anolyte might possibly be tolerated. However, when sulfuric acid is employed in the catholyte of the electrodialysis process the concentration of sulfate ions in the anolyte increases rapidly to the point at which the ratio of chromic acid to sulfuric acid in the chromium plating solution falls below the minimum permissible ratio of 40:1.

The build-up of mineral acid anions in the chromium plating solution when a mineral acid is employed in the catholyte of the electrodialysis process is illustrated by the following table which sets forth the results obtained when chromium plating solutions of various chromic acid content were subjected to electrodialysis with a catholyte comprising a 10% solution of sulfuric acid:

TABLE 1

Run	CrO ₃ (g/l)	Ratio - CrO ₃ :H ₂ SO ₄		Length Of Run
		At Start	At End	
1-A	177.5	79:1	58:1	3½ hrs.
1-B	244.4	88:1	41:1	13½ hrs.
1-C	224.0	85:1	30:1	21 hrs.
1-D	202.4	87:1	26:1	30 hrs.

In all of the above runs the ratio of chromic acid to sulfuric acid in the chromium plating solution was severely upset by a relatively short dialysis time by reverse migration of sulfate anions from the catholyte to the plating solution.

As a result of my investigations into the problem of build-up of harmful anions in the chromium plating solution, I have discovered that if certain ionizable organic compounds (for example, certain carboxylic acids) are employed as the electrolyte in the catholyte of the process there is no significant build-up of harmful anions of any kind in the plating solution. In general, the anion of the organic compound employed in the catholyte must either be intrinsically harmless or be capable of being converted to harmless reaction products when introduced into the chromium plating solution. More particularly, the anion of the ionizable organic compound must be capable of being oxidized to harm-

less oxidation products (for example, carbon dioxide that evolves from the solution) and water when reacted with chromic acid. The build-up of harmful anions in the anolyte may be inhibited by the relatively large size of the organic anions in the catholyte which do not move as freely through the permeable membrane into the anolyte as do the somewhat smaller mineral acid anions. However, the principal factor in the avoidance of buildup of anions in the anolyte is the fact that those organic anions that do pass through the membrane into the anolyte are immediately oxidized by chromic acid to oxidation products that do not harm the anolyte. (The term "harmless oxidation products" as employed herein and in the appended claims refer to products that do not adversely affect the quality of the chromium deposit when the anolyte is subsequently employed as the electrolyte in a conventional chromium plating process).

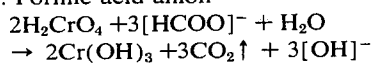
My investigations have also established that many potentially useful organic compounds are not sufficiently soluble or sufficiently ionizable in water to serve as an effective electrolyte material in the catholyte. Specifically, I have found that the organic compounds employed in the catholyte must be sufficiently soluble in water so that the concentration of these compounds in the catholyte is at least 1 Normal. (A 1 Normal solution contains 1 gram molecular weight of the dissolved compound divided by the hydrogen equivalent of the compound in each liter of the solution). I have also found that the ionic dissociation of the organic compounds in the catholyte must be sufficient so that the conductivity of the catholyte is at least 1.0×10^{-4} mho/cm. Solutions of organic compounds of lower solubility or lower conductivity are unsatisfactory electrolytes and are not useful as catholytes in the electrodialysis process of the invention.

Many organic compounds having the requisite solubility and ionizability (for example, certain sulfonated, phosphated or chlorinated organics) are not useful in the catholyte of the process because they form harmful reaction products (such as sulfate, phosphate or chloride anions) when reacted with chromic acid in the anolyte. On the other hand, many potentially ionizable organic compounds that do not form harmful oxidation products (for example, the higher fatty acids, the higher substituted α -hydroxy fatty acids, most polycarboxylic acids and the aromatic acids) are not sufficiently soluble in water to be useful in the catholyte, and many soluble organic compounds (for example, the lower aliphatic alcohol and the polyaminomonocarboxylic acids) are not sufficiently ionizable to be useful in the catholyte of the process.

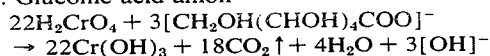
Ionizable organic compounds that have the requisite solubility and conductivity when employed in the catholyte of the process and that do not form harmful reaction products when reacted with chromic acid in the anolyte include, but are not limited to, saturated aliphatic monocarboxylic acids having from 1 to 5 carbon atoms, substituted α -hydroxy fatty acids having 2 to 7 carbon atoms, aliphatic dicarboxylic acids having 2, 3 or 5 carbon atoms, and aliphatic tricarboxylic acids and amino acids of the requisite solubility and conductivity. One or more of these ionizable organic compounds may be present in the catholyte in the form of the free acids of water soluble salts of the acids or both. The anion of all of these ionizable compounds will react with chromic acid to form gaseous oxidation products

(for example, carbon dioxide) and water in accordance with the following representative equations.

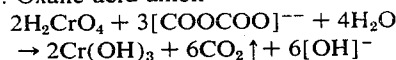
1. Formic acid anion



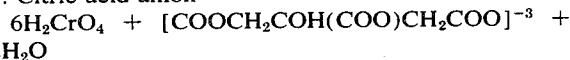
2. Gluconic acid anion



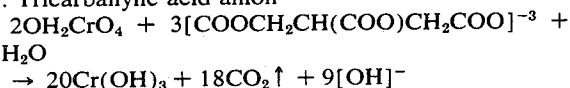
3. Oxalic acid anion



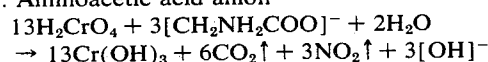
4. Citric acid anion



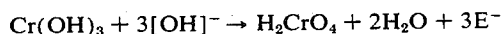
5. Tricarballic acid anion



6. Aminoacetic acid anion



Trivalent chromium is conventionally represented as chromic hydroxide ($\text{Cr}(\text{OH})_3$) in the above equations although it is probable that neither this compound nor the hydroxide ions are actually present as such in the acidic chromium plating solution comprising the anolyte of the process. Moreover, as previously noted, trivalent chromium introduced into the anolyte from the chromium plating process or produced in situ in the anolyte in accordance with the foregoing equations is electrolytically oxidized to the hexavalent state in the anolyte in accordance with the following representative equation:



The highly oxidized metal cations which migrate from the anolyte into the catholyte tend to be electrolytically reduced to lower valent forms or to the metal itself under the reducing conditions which prevail in the catholyte. In particular, copper ions tend to be reduced to metallic copper which precipitates in finely divided form from the catholyte, and ferric ions tend to be reduced to ferrous hydroxide which also precipitates from the catholyte solution. Both precipitates can be troublesome if allowed to build up in the cell and in the tubing and pump associated therewith. Accordingly, it is highly desirable either to maintain these metal cations in solution in the catholyte or to remove them from the catholyte by filtration or the like. To this end the catholyte advantageously contains a chelating agent for the metal cations introduced therein to from the anolyte. Some of the ionizable organic compounds employed as the electrolyte in the catholyte are themselves excellent chelating agents for these metal ions. For example, ammoniated citric acid (and in particular, citric acid partially neutralized with ammonium hydroxide to a pH of from about 6 to 7) forms very stable water soluble complexes with ferric ions, and alkaline sodium gluconate (and in particular, gluconic acid reacted with an excess of sodium hydroxide to a pH of at least 12) forms very stable complexes with both iron and copper. Oxalic and tartaric acids and their salts also form stable complexes with copper and iron. In addition, known chelating agents such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA) and diethylenetriaminepentaacetic (DTPA)

acid may be added independently to the catholyte solution to augment or supplant the chelating properties of the organic electrolyte. In addition, a filter is advantageously provided to remove any metallic particles

anolyte, the degree of reoxidation of trivalent chromium (Cr^{+3}) to hexavalent chromium, and the degree of removal of iron from the anolyte for each run are set forth in Table 3.

TABLE 3

Run No.	Length of Run Hours	Electricity		Total Kwh	Chromic Acid (g/l)	Ratio $\text{CrO}_3:\text{SO}_4$		Trivalent Chromium*		Iron		Iron Removed Percent
		Current Volts	Amps.			Start	End	Start	End	G/L Start	G/L End	
2A	44.25	20	90	79.6	238.6	84:1	106:1	2.4	0.8	3.41	2.56	24.9
2B	46.5	13	136	81.2	247.8	50:1	51:1	—	—	4.25	2.63	38.1
2C	48	9.8	136	76.9	238.3	96:1	94:1	3.1	0.3	6.76	2.38	64.8
2D	29.5	10.2	136	40.9	249.5	88:1	91:1	4.0	0.0	5.90	1.97	66.0
2E	42.5	12.4	136	71.6	225.2	94:1	106:1	2.9	0.0	4.89	2.28	53.3

* Cr^{+3} grams/liter (G/L)

which may precipitate from the catholyte solution being circulated through the electro dialysis cell.

The following examples are illustrative but not limitative of the practice of the invention.

EXAMPLE I

Five representative chromium plating solutions contaminated with various amounts of copper and iron ions were purified by electro dialysis in an electro dialysis cell similar in its basic configuration to the cell hereinbefore described. Two pairs of anolyte and catholyte compartments were provided, and both of the electrolyte solutions and the electrolyzing current flowed in parallel through the cell compartments. The electrodes were stainless steel and the cation permeable membrane was made of perfluorosulfonic acid resin. The catholytes in each case comprised an aqueous solution of citric acid partially or completely neutralized with ammonium hydroxide (ammoniated citric acid) having the normality (N), conductivity (mho/cm) and hydrogen ion concentration (pH) set forth in Table 2. In two cases (Runs 2D and 2E) a small amount (about 35 grams per liter) of a chelating agent for copper, triethanolamine (TEA), was added to the catholyte.

TABLE 2

Run No.	Catholyte Composition	N	mho/cm ($\times 10^{-4}$)	pH
2A	Ammoniated Citric Acid	4.5	2.25	6.2
2B	Ammoniated Citric Acid	6.9	2.4	5.2
2C	Ammoniated Citric Acid	10.2	2.6	6.0
2D	Ammoniated Citric Acid TEA	8.9	2.2	7.6
2E	Ammoniated Citric Acid TEA	8.9	2.3	6.2

The electrolytic conditions employed, the composition of the various chromium plating solutions, the ratio of chromic acid to sulfuric acid ($\text{CrO}_3:\text{SO}_4$) in the

There was no build-up of harmful anions in any of the chromium plating solutions referred to in Table 3. Substantially all of the trivalent chromium present in each solution was oxidized to the hexavalent state, and there was a substantial reduction in the amount of iron present in the chromium plating solution as a result of the electro dialysis of these solutions. Runs 2C, 2D and 2E were more efficient than runs 2A and 2B in the removal of iron, in part a reflection of the higher starting concentrations of iron in the last three chromium plating solutions.

EXAMPLE II

Eight representative chromium plating solutions contaminated with various amounts of copper and iron ions were purified by electro dialysis in the cell employed in Example I. The catholytes employed in this series of runs comprised aqueous solutions of several different ionizable organic compounds, and combinations thereof, the composition of which, the normality (N) of which, the conductivity (mho/cm) of which and the pH of which are set forth in Table 4.

TABLE 4

Run No.	Catholyte Composition	N	mho/cm ($\times 10^{-4}$)	pH
3A	Ammoniated Citric Acid	10.5	2.3	6.5
3B	Ammoniated Citric and Gluconic Acids	7.6	2.6	6.5
3C	Same as 3B	7.6	2.6	6.5
3D	Ammoniated Citric Acid and Ammonium Oxalate	10.6	2.1	6.5
3E	Same as 3D	10.6	2.1	6.5
3F	Sodium Gluconate Sodium Hydroxide	8.2	2.8	>12
3G	Same as 3F	8.2	2.8	>12
3H	Ammoniated Citric and Formic Acids	16.6	3.4	6.5

The electrolytic conditions employed, the composition of the various chromium plating solutions, and the degree of removal of iron and copper from the anolyte for each run in this series are set forth in Table 5.

TABLE 5

Run No.	Length Of Run Hours	Electricity		Total Kwh	Chromic Acid (G/L)	Copper		Copper Removed Percent	Iron		Iron Removed Percent
		Current Volts	Amps			G/L Start	G/L End		G/L Start	G/L End	
3A	23	8	136	25.02	245	6.30	2.73	56.7	3.90	3.08	20.9
3B	18.5	10.3	136	25.9	237	6.40	2.89	54.9	3.90	3.09	20.8
3C	20.0	10.0	136	27.2	256	6.70	3.06	54.3	4.20	3.57	14.9
3D	7.5	7.6	136	7.75	249	6.50	4.71	27.5	4.10	3.60	12.1
3E	17.5	8.4	136	20.0	219	5.90	2.40	40.7	3.90	3.03	22.4
3F	32.75	9.2	136	41.0	443	0.60	0.29	51.7	6.40	5.43	15.0
3G	25	9.6	136	32.6	209	3.00	1.26	42.1	1.80	1.44	19.8
3H	48	6.0	136	39.2	261	3.90	0.88	77.4	2.30	1.59	30.9

As shown in the foregoing table, electro dialysis of impure chromium plating solutions with catholytes containing a variety of water soluble ionizable organic compounds resulted in the removal from the anolyte of a substantial proportion of the copper and iron content of these plating solutions. There was no build-up of harmful anions in the anolyte. The degree of removal of copper from the chromium plating solutions was excellent despite the relatively short duration of the electro dialysis runs. The somewhat lower degree of removal of iron is, in part, a reflection of the relatively low starting concentration of iron in these plating solutions as well as the relatively short duration of the runs.

From the foregoing description of the electro dialysis process of the invention it will be seen that I have made an important contribution to the art to which the invention relates.

I claim:

1. In the process for removing dissolved metallic cation contaminants from an aqueous solution of chromic acid by electro dialysis in an electro dialysis cell having an anolyte compartment containing an anode and a catholyte compartment containing a cathode, said anolyte and said catholyte compartments being separated by a cation permeable membrane, in which process the contaminated chromic acid solution is contained in said anolyte compartment and comprises the anolyte of said cell, an aqueous solution of an ionized electrolyte is contained in said catholyte compartment and comprises the catholyte of said cell, and an electric current is passed between said anode and said cathode through said anolyte and said catholyte to cause contaminating metal cations to migrate from the anolyte through the cation permeable membrane into the catholyte, the improvement which comprises employing as the catholyte an aqueous solution of at least one water soluble ionizable organic compound the anions of which are oxidized to harmless oxidation products and water when reacted with the chromic acid-containing anolyte, the solubility of said ionizable organic compounds being such that the total con-

centration thereof in the catholyte is at least 1 Normal and the ionic dissociation of said organic compounds being such that the conductivity of the catholyte is at least 1.0×10^{-4} mho/cm.

2. The process according to claim 1 in which the catholyte contains a chelating agent for the contaminant metal ions transferred thereto from the anolyte.

3. The process according to claim 1 in which the water soluble ionizable organic compound comprises a saturated aliphatic carboxylic acid having 1 to 5 carbon atoms.

4. The process according to claim 1 in which the water soluble ionizable organic compound comprises a substituted α -hydroxy fatty acid having 2 to 7 carbon atoms.

5. The process according to claim 4 in which the organic compound comprises gluconic acid reacted with sodium hydroxide to a pH of at least 12.

6. The process according to claim 1 in which the water soluble ionizable organic compound comprises an aliphatic dicarboxylic acid having 2, 3, or 5 carbon atoms.

7. The process according to claim 1 in which the water soluble ionizable water compound comprises citric acid reacted with ammonium hydroxide to a pH of from about 5.2 to about 7.6.

8. The process according to claim 7 in which the ammoniated citric acid solution has a pH of from about 6 to 7.

9. The process according to claim 1 in which the water soluble ionizable organic compounds comprise a mixture of ammoniated citric and gluconic acids.

10. The process according to claim 1 in which the water soluble ionizable organic compounds comprise a mixture of ammoniated citric acid and ammonium oxalate.

11. The process according to claim 1 in which the water soluble ionizable organic compounds comprise a mixture of ammoniated citric and formic acids.

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