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METHOD OF PREVENTING ETCH ON STEEL AND IRON IN PLATING BATHS

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17 Claims

ABSTRACT OF THE DISCLOSURE

A process for electroplating a plate onto a steel or iron cathode having areas of low cathode current density whereon plating does not occur and selected areas of high cathode current density which comprises placing an auxiliary electrode adjacent to the cathode areas of low cathode current density, said electrode being connected to a variable power supply source; maintaining the low current density areas of said cathode anodic with respect to said auxiliary electrode, and plating the plate onto said selected areas of said cathode, the cathode areas of low current density remaining substantially free of etching during said plating; the auxiliary electrode may be coated with metal in low hydrogen overvoltage state.

This application is a continuation of Ser. No. 291,925, filed July 1, 1963, now abandoned.

This invention relates to plating and more particularly to a technique for preventing etching of steel cathodes at cathodic areas of low current density.

As is well known to those skilled in the art, electroplating of various metals, typically nickel, copper, tin, zinc, or chromium may be effected in baths of varying acidity and composition; many of these baths may contain chloride or fluoride together with oxidizing agents which may be an integral part of the bath or present as an additive. During plating of basis metals in such baths, it is necessary to control current density over the areas to be plated. Because of differences in areas or geometry or accessibility, there may be portions of the cathode which have a current density low enough so that plating is not expected to and in fact does not occur. It has been found, particularly when the bath is acid and contains e.g. chloride or fluoride ions together with oxidizing agents, that in these low current density areas, etching is a problem. Specifically the surface of these unplated areas may be corroded during plating operations sufficiently to alter the dimensions substantially and/or to spoil the appearance of the finished article. The problem of etching may be present in various baths, typified by chromium plating baths, nickel plating baths, acid copper baths, acid tin baths, acid zinc baths containing halides or halide-complexes and frequently containing oxidizing agents, etc.; for purposes of convenience, reference will hereinafter be made to chromium plating baths.

As is well known to those skilled in the art, chromium plating for example may be effected by use of a bath containing chromic acid and sulfate or sulfate together with other compounds which may be employed to effect various desirable results. Typical of these additives compounds may be fluorides or fluoride complexes.

Other illustrative chromium plating systems may include soluble catalyst systems containing e.g. chromic acid and sulfate such as sulfuric acid in amount sufficient to give the desired concentration of sulfate ion, or self-regu-

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lating baths, typically those containing silicofluorides together with sulfate.

During plating of chromium onto steel and iron from baths typified by the foregoing, it is common to operate at a temperature which may vary depending upon the concentration of CrO_3 . Commonly however the temperature of operation may be 34°C .– 72°C . and typically 48°C .– 63°C . The cathodic current density may preferably be controlled to fall in the range of 8–100, and typically 12–50 amperes per square decimeter on the selected areas of high current density whereon plating may occur. However, because of the irregular shape of many pieces which are to be chromium plated, it is not possible to maintain uniform desired current density over the entire piece. If the current be set to provide a current density as noted, there will be places, typically interior portions, end portions, back portions, or crevices where the current density may be considerably lower, for example 2.0 or less and frequently 0.1–1.0 ampere per square decimeter.

It has been found that these areas of low current density of the steel and iron cathodes are strongly etched during plating and especially so when the bath is a chromium plating bath which contains fluoride or silicofluoride ions which may be present in self-regulating high speed baths, soluble catalyst baths, or sparingly soluble catalyst chromium plating baths. In order to eliminate this etching in chromium plating systems, it has heretofore been common to coat with insulating coatings, tapes, or waxes those portions of the cathode where low current density is anticipated. The use of such techniques is time-consuming and expensive. Tapes or waxes must be carefully placed and removed since any holes or spaces (including edge areas which may be undermined) in the protective covering will allow severe etching of the so-exposed metal to take place. Such coatings, tapes, or waxes may be expensive to purchase and apply. Various other attempts to minimize low current density etching of cathodes in the noted plating baths have not been uniformly successful and there is today no economical etch preventive system which is completely satisfactory.

It is an object of this invention to provide a technique for preventing undesirable etching of steel and iron in plating operations including e.g. chromium and other corrosive plating operations. Other objects will be apparent to those skilled in the art on inspection of the following description.

In accordance with certain of its aspects, the process of this invention for electroplating a plate metal onto a cathode, selected from the group consisting of steel and iron, having areas of low cathode current density and selected areas of high cathode current density, comprises placing an auxiliary electrode adjacent to the cathode areas of low cathode current density whereon plating does not occur; maintaining said auxiliary electrode cathodic with respect to the low current density areas of said cathode whereby said low current density areas of said cathode are maintained anodic with respect to said auxiliary electrode; and plating the plate metal onto said selected areas of the surface of said cathode, the said cathode areas of low current density remaining substantially free of etching during said plating.

Typical of the plate metal with which the process of this invention may find use may be the aforementioned chromium plate including hard chromium plate. This invention will be especially suitable for use with the noted chromium plating baths, including the soluble or sparingly soluble catalyst-containing chromium plating baths, since it is with these baths that the problems of etching

may be most severe because of the presence of chloride, fluoride, or silicofluoride ions in the bath. The cathodes which may be used in the practice of this invention may be those steel and iron articles upon which a plate, typically a chromium plate is desired.

The steel cathodes with which this invention particularly finds use may include alloys which are commonly identified as steel. Steel thus includes those iron-containing alloys which may contain carbon in amount intermediate between the low levels of wrought iron and the high level of cast iron. Typically, as is well known, steel may for example contain carbon in amount of about 0.10%–0.40%, and more commonly 0.15%–0.25% depending on the type of steel. Other materials including e.g. manganese, nickel, silicon, molybdenum, chromium, etc. may be present in steel. It is a particular feature of this invention that an iron (i.e. a pure iron such as wrought iron) cathode may be protected in the manner herein disclosed. These steel and iron basis metals may be characterized by high susceptibility to etching at low current density areas during e.g. chromium plating particularly when the baths employed are fluoride-containing chromium plating baths.

The auxiliary electrode may be fabricated of any convenient metal which will not dissolve in or be otherwise appreciably affected by the solution during the plating operation. It may be for example nickel; lead; chromium; noble metals including platinum, palladium, gold, silver, rhodium, ruthenium, iridium; and carbon. Preferably it will be formed of steel.

In the preferred embodiment the auxiliary electrode may be steel, the surface of which may have been previously treated to minimize or eliminate (a) corrosion of the metal; and (b) plating with resultant gain of dimension.

Preferably the surface of the auxiliary electrode on which corrosion or plating might occur may be at least partially stopped-off with a non-conductive coating such as lacquer, waxes, or tapes, while other parts of the electrode are conductive and protected by being placed in intimate electrical contact with a low hydrogen overvoltage metal in an active, finely divided surface condition. Such low hydrogen overvoltage metals may include platinum, palladium, rhodium, gold, iridium, and nickel.

In practice of this invention, the auxiliary electrode may be placed adjacent to the cathode areas of low current density. Such areas, as will be apparent to those skilled in the art, may be e.g. rear or recessed areas of the cathode or inside areas of the cathode. Preferably the auxiliary electrode may be placed quite close to the low current density cathode areas noted and as far away from the high current density cathode areas as is conveniently possible. The auxiliary electrode may preferably be shaped to permit positioning close to the noted areas. Preferably it may have the same configuration as the areas adjacent to which it is to be positioned.

Preferably selected portions of the surface of the auxiliary electrode may be masked or stopped-off to provide control of the current flow between the auxiliary electrode and the cathode. This treatment may permit proper superimposition of the counter-cathodic current over the etching current which might otherwise etch the low current density areas on the cathode.

Preferably the auxiliary electrode may be maintained cathodic to the lower current density areas of the cathode so that the current may flow from the low current density areas of the plating cathode to the auxiliary electrode thus making the low current density areas anodic. This may be effected by placing the auxiliary electrode in an auxiliary circuit which includes an auxiliary power supply which is electrically connected to the cathode through a D.C. ammeter which may measure the direction and flow of current in the auxiliary circuit. The auxiliary power supply may be adjusted or set so that the flow of current in the chromium plating solution may be from

the low current density area of the cathode to the auxiliary electrode. This insures that the low current density areas may be protected from etching by being made anodic at controlled potential.

The potential of these low current density areas, occurring e.g. in the inside of a pipe, may be determined by means of a reference electrode, typically a saturated calomel electrode, which may be fixed in position preferably as close as possible to the low current density areas, without actually making an electrical connection. The potential of the noted areas may thus be measured. Preferably the low current density areas may be maintained anodic primarily by noting from the ammeter that the current in the external circuit is flowing in the proper direction.

In an illustrative embodiment of the process of this invention, as shown in the attached drawing, a plating solution 10 may be maintained in vessel 11 which contains a cylindrical cathode piece generally designated 12 to be electroplated on the outside surface 13. Plating anodes 14 and 15, also suspended in solution 10 by standard means similar to that supporting cathode 12, may be in a plating circuit which includes conductors 16, joined to anodes 14 and 15, main power supply 17, and conductor 18 joined to cathode 12. There may also be suspended in the solution 10 the auxiliary electrode generally designated 19 which preferably in this embodiment may be concentric to the low current density areas 20 of cathode 12.

Most of the etching occurs at current densities just below where plating stops and less etching occurs at the extreme low current densities; thus in this embodiment the center 21 of the length of the auxiliary cathode 19 may have been masked or stopped-off by a commercial masking or stop-off tape. The conducting end portions 22 are untreated with stop-off composition or tape, but if desired they may be treated to minimize etching or plating by the technique hereinbefore disclosed. It will be appreciated that these treatments of the electrode 19 may be optional. The auxiliary electrode 19 may be in an auxiliary circuit which may include conductor 23, ammeter 24, voltmeter 31, auxiliary power supply 25, and conductor 26; the latter may be connected as shown to conductor 18.

Preferably the reference cell 27, positioned as shown as close as conveniently possible to the low current density area 20 of cathode 12, may be connected through conductor 28, voltmeter 29, and conductor 30 to plating cathode 12.

In one series of examples using the apparatus of the drawing, the cathode 12 was a steel pipe of type 1015 steel 19.5 cm. long, 4.4 cm. outside diameter, and 0.3 cm. wall thickness. The auxiliary cathode 19 was a type 1015 steel cylindrical rod having a diameter of 1.25 cm. This cathode 19 was stopped-off at each end with masking tape over areas 21a so that the current would not leak to the outside of cathode 12, and areas 22 were treated by painting with a solution (containing 2.5 g./l. chloroplatinic acid, $H_2PtCl_6 \cdot H_2O$, plus water to make up one liter) for 5 seconds followed by rinsing with water, thereby producing a low hydrogen overvoltage layer of platinum over areas 22. This assembly was placed in a chromium plating solution 10 containing 225 g./l. chromic acid, 2.2 g./l. silicofluoride ion (added as K_2SiF_6) and 1.08 g./l. sulfate ion (added as sulfuric acid).

The main power supply was set to provide a current density of 40 amps/dm.² based on the outside area 13 of cathode 12. During the course of these tests, the auxiliary power supply was varied to provide different voltages across auxiliary cathode 19 and the low current density areas 20 of cathode 12, while the plating current was maintained constant at 40 amperes per square decimeter.

In each experiment, the cathode 12 was removed at the end of one hour and the pipes cut open for inspection. The results are shown in the table.

TABLE

Expt.	Applied voltage	LCD potential (volts)*	Width of etch bands (cm.)
1-----	0	-0.9	9.75
2-----	0.5	-0.5	2.5
3-----	1.0	-0.5	1.2
4-----	2.0	+0.2	0.6
5-----	2.5	+0.6	0

*The LCD potential is the potential of the low current density areas of the plating cathode, measured with respect to standard saturated calomel electrode at constant bath temperature of 55° C.

As may be seen from the table, as the applied voltage (from the auxiliary power source 25) between the cathode 12 and the auxiliary electrode 19 increases from 0 to 2.5 volts, and the LCD anodic potential measured by the voltmeter 29 increases from -0.9 volt to +0.6 volt, the width of the etch bands at each end of the cathode pipe 12 decreased from 9.75 cm. (i.e. etching over the entire inside area of the pipe) down to 0 cm. (i.e. no etching at all). More specifically it may be observed that the cathode 12 may be satisfactorily plated with chromium with little-to-no etching on the inner or low current density areas 20. It will be apparent that the applied voltage which may be employed will not be appreciably higher, and preferably it will be equal to the value (in this case 2.5 volts) which generates an anodic LCD potential sufficiently high (above about 0 volt with respect to saturated calomel electrode) so that the cathode 12 becomes anodically protected in the low current density areas 20. At potentials more positive than 0.6 volt, complete protection was achieved.

In another series of examples, two identical pieces of pipe (one a control piece and one an experimental piece) each 19.5 cm. long, 6.4 cm. outside diameter, and 0.6 cm. wall thickness, otherwise identical to the above specimens, were chromium plated under conditions identical to the conditions of the first series of examples except as hereinafter noted. The experimental piece was plated under an auxiliary applied voltage which yielded an anodic potential on the low current density areas of +0.5 volt. The control piece did not make use of the auxiliary electrode; it was plated under the same applied voltage.

After one hour, it was found that the inside of the plated control piece was very badly etched over its entire area and had etch bands at each end of about 9.75 cm. The experimental piece was found to be substantially free of etching and had substantially non-existent etch bands.

As many embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention includes all such modifications as come within the scope of the appended claims.

What is claimed is:

1. The process for electroplating from an aqueous acid bath onto a cathode selected from the group consisting of steel and iron, having areas of low cathode current density whereon plating does not occur and etching tends to occur and selected areas of high cathode current density which comprises placing an auxiliary electrode adjacent to the cathode areas of low cathode current density, said electrode being connected to a variable power supply source; maintaining the low current density areas of said cathode anodic with respect to said auxiliary electrode; and electroplating the plate onto said selected areas of the surface of said cathode, the said cathode areas of low current density remaining substantially free of etching during said electroplating.

2. The process of claim 1 wherein said cathode is a steel cathode.

3. The process of claim 1 wherein said cathode is an iron cathode.

4. The process of claim 1 wherein said plate is selected from the group consisting of chromium, nickel, copper, tin, and zinc.

5. The process of claim 1 wherein said plate is chromium plate.

6. The process of claim 1 wherein said auxiliary electrode is a steel electrode.

7. The process for electroplating a plate onto a cathode selected from the group consisting of steel and iron, having areas of low cathode current density whereon plating does not occur and selected areas of high cathode current density which comprises placing an auxiliary electrode adjacent to the cathode areas of low cathode current density, said electrode being connected to a variable power supply source and coated with a low hydrogen overvoltage metal selected from the group consisting of platinum, palladium, rhodium, gold, iridium and nickel, the coating on said auxiliary electrode being applied by contacting said electrode with an ionic compound of said metal thereby depositing said coating on said electrode; maintaining the low current density areas of said cathode anodic with respect to said auxiliary electrode; and electroplating the plate onto said selected areas of the surface of said cathode, the said cathode areas of low current density remaining substantially free of etching during said electroplating.

8. The process of claim 7 wherein said metal is deposited chemically.

9. The process of claim 7 wherein said metal is deposited electrolytically.

10. The process of claim 7 wherein said plate is chromium plate and said cathode is a steel cathode.

11. The process of claim 10 wherein the chromium is electrodeposited from an aqueous chromic acid bath containing sulfate ions and complex fluoride ions.

12. The process of claim 7 wherein the low hydrogen overvoltage metal is platinum.

13. The process of claim 7 wherein the low hydrogen overvoltage metal is palladium.

14. The process of claim 7 wherein the low hydrogen overvoltage metal is rhodium.

15. The process of claim 7 wherein the low hydrogen overvoltage metal is gold.

16. The process of claim 7 wherein the low hydrogen overvoltage metal is iridium.

17. The process of claim 7 wherein the low hydrogen overvoltage metal is nickel.

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