

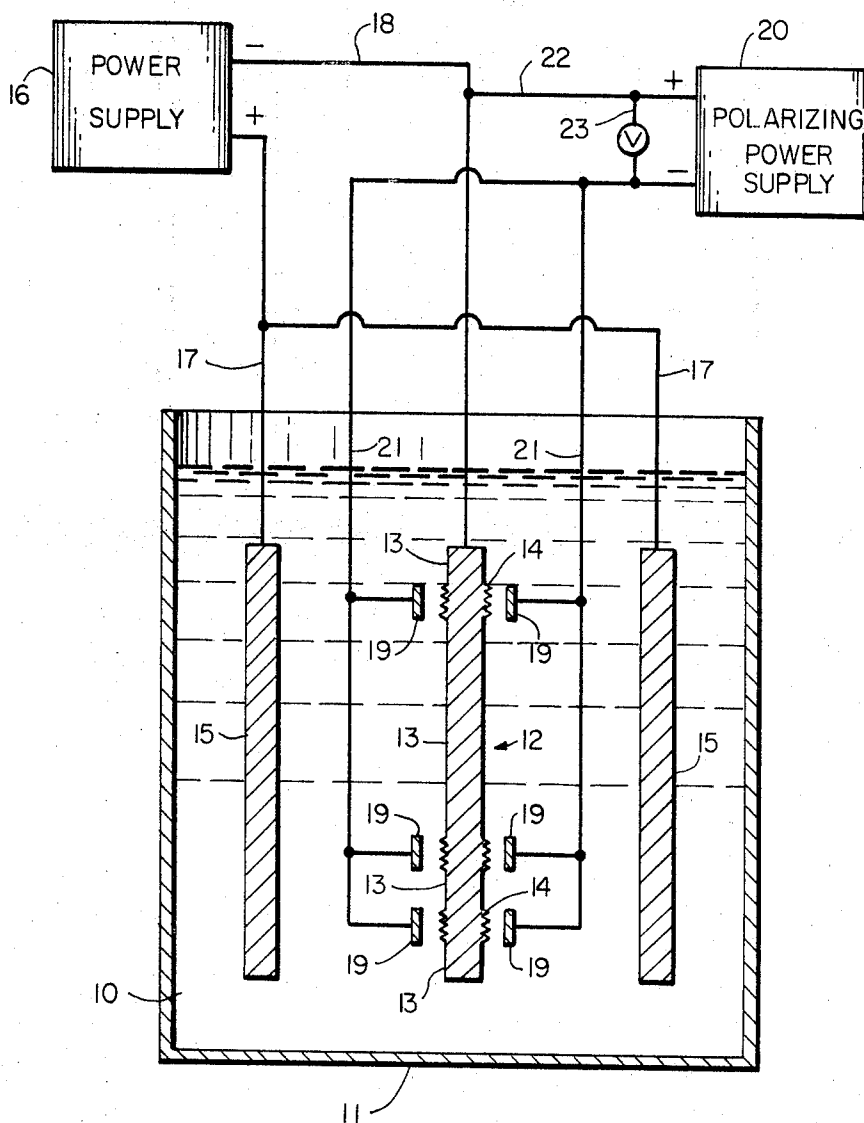
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METHOD OF STOPPING-OFF PLATING IN ELECTROPLATING BATHS

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METHOD OF STOPPING-OFF PLATING IN ELECTROPLATING BATHS

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2 Claims

ABSTRACT OF THE DISCLOSURE

A process for electroplating a plate metal from a bath onto a cathode having predetermined areas to be plated and selected areas to be stopped off which comprises placing an auxiliary electrode adjacent to said selected areas, maintaining said selected areas anodic to said auxiliary electrode and subjecting said cathode to plating current density whereby said metal is deposited on the said predetermined areas and said selected areas remain stopped off, and an apparatus for electroplating which comprises an electroplating bath, at least one anode therein, a cathode having predetermined areas to be plated and selected areas to be stopped off, an auxiliary electrode adjacent to each of the said selected areas of said cathode, a main power supply establishing a potential across the anode and the cathode, and means for maintaining said selected areas anodic to said auxiliary electrode. In one embodiment, the means for maintaining said selected areas anodic to said auxiliary electrode includes a polarizing power supply establishing a potential between selected areas of the cathode and the auxiliary electrode, the positive terminal of the polarizing power supply being joined to the negative terminal of the main power supply. The auxiliary electrode may contain a thin coating of platinum sufficient to substantially inhibit electroplating of said auxiliary electrode.

This application is a continuation of application S.N. 291,987, filed July 1, 1963, now abandoned.

This invention relates to a method of electroplating and more particularly to a method of stopping-off selected areas of electrodes to permit control of these selected areas so that they may be free from plate which is to be deposited on other areas of the electrode.

As is well known to those skilled in the art, metals may be immersed in various baths in the course of different treating processes wherein a desired portion of the metal may, for example, be subjected to electroplating. 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 which may be an integral part of the bath or present as an additive. Because of differences in area or geometry or accessibility, there may be predetermined portions of the cathode which are to be plated and selected areas on which a plate is not desired. The surface of these selected areas, if not properly treated to prevent plating thereon, i.e. if not stopped-off, may undesirably be plated sufficiently to alter the dimensions substantially and/or to spoil the appearance of the finished article. The problem of stop-off may be present in various baths, typified by chromium plating baths, nickel plating baths, acid copper baths, acid tin baths, zinc baths containing halides or halide-complexes, etc.; for purpose of convenience, reference will hereinafter be made to chromium plating baths.

Commonly the areas of the cathode on which plate is not desired may be covered or painted with a masking or stop-off material which prevents deposition and build-

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up of the plate on these high current density areas which would normally be plated. The masking or stop-off coatings are commonly subjected to severe corrosive conditions for an extended period of time. For example, in chromium plating these materials may remain in position for extended periods of time, often for days, under the most severe oxidizing conditions in contact with baths which may contain sulfuric acid and chromic acid together with numerous other chemicals. Furthermore the stop-off material may be subjected to the highly erosive effect of the hydrogen which is liberated.

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 together with other compounds which may be employed to effect various desirable results. Typical of these additive 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-regulating baths, typically those containing silicofluorides together with sulfate.

During chromium plating from baths typified by the foregoing, it is common to operate at a temperature which may vary depending upon the type and purpose of the plating operation. 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 a.s.d. (i.e. amperes per square decimeter) on the selected areas of high current density whereon plating may occur. However, because there may be certain selected high current density areas which are not to be chromium plated, it is desired to stop-off these areas.

In chromium plating systems, it has heretofore been common to coat with tapes or waxes those selected portions of the cathode where no plate is desired. 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 coating will allow plating of the so-exposed metal to take place. Such tapes or waxes may be expensive to purchase and apply. Various other attempts to stop-off selected areas of cathodes in the noted plating baths have not been uniformly successful, and there is today no economical, commercial stop-off system which is completely satisfactory from the production point of view.

Various other processes are also known, including chemical treating, etching of selected portions of a piece, anodizing of pieces, etc. where it is desired to protect certain portions of the workpiece from the action of the solution. Stop-off materials to effect these results have heretofore been either paints or tapes. Typical paints may include plastic materials such as polymers of vinyl chloride or vinyl acetate which may contain plasticizers, pigments, solvents, etc. These may be applied by painting onto the desired portions of the workpiece which are not to be subjected to the action of the solution. Masking tapes which may be employed for the same purpose may be wrapped around the piece and cover the areas which are to be protected or stopped-off.

As is well known to those skilled in the art, application of e.g. masking tapes and paints is a time consuming and expensive job. Furthermore, many of the stop-off paints or tapes are unsatisfactory in that, during plating, they may become pervious to the solution or not adherent to the workpiece. Perviousness permits growth of dendritic trees at or adjacent to the tape or paint; such growths must be removed by grinding or machining to make the part satisfactory with respect to appearance and dimensionality. It is a particular objection that tapes and

paints permit build-up of the plate at the point immediately adjacent to the non-conducting tape or paint and thus may require a grinding operation, after plating is complete, to remove the ridges which may be present. It is a further objection that paint or masking tape must be removed from the workpiece at the completion of the plating operation. This may typically be done by cutting, peeling, scraping, by action of solvents, etc.

It is an object of this invention to provide a novel technique for masking or stopping-off areas to be maintained free of a deposited plate during plating. Other objects will be apparent to those skilled in the art on inspection of the following detailed description.

In accordance with certain of its aspects, the process of this invention for electroplating a plate metal from a bath onto a cathode having predetermined areas to be plated and selected areas to be stopped-off comprises placing an auxiliary electrode adjacent to said selected areas, maintaining said selected areas anodic to said auxiliary electrode, and subjecting said cathode to plating current density whereby said plate metal is deposited on the said predetermined areas and said selected areas remain stopped-off.

In practice of this invention, the selected areas to be stopped-off may be stopped-off by placing adjacent thereto an auxiliary electrode. The metal from which the auxiliary electrode may be fabricated may be any convenient or available metal typically iron, steel, etc. Preferably the auxiliary electrode may be formed of a metal which possesses a high degree of resistance to the plating bath under the conditions of operation. In a preferred embodiment the auxiliary electrode may be stopped-off by any conductive means which will minimize or eliminate electrodeposition thereon of the metal being plated, while simultaneously permitting current flow thereto.

In a preferred embodiment of this invention, the auxiliary electrode may be stopped-off by means of the technique disclosed in applicant's copending patent application. Typically such stopping-off of the auxiliary electrode may be effected by immersing the auxiliary electrode in a solution of e.g. platinum chloride, sodium chloride, and hydrochloric acid sufficient to lower the pH to about 1.5, whereby the auxiliary electrode may become immersion plated with a thin coating of platinum. This thin coating of platinum may be sufficient to eliminate electroplating of metal e.g. chromium on the auxiliary electrode during practice of the instant invention, but it will not interfere with the flow of current from the auxiliary electrode.

In practice of the invention, the auxiliary electrode, preferably treated as hereinbefore disclosed, may be placed within the electroplating solution adjacent to the selected areas whereon plating is not desired. Preferably the auxiliary electrode will be of size, shape, and configuration to substantially cover the entire selected area. Typically the auxiliary electrode will conform to the said selected areas. Where the selected areas are spaced from each other, the auxiliary electrode may be composed of several independent auxiliary electrode pieces electrically connected to each other and to the auxiliary electrode circuit as hereinafter described in detail. Preferably the auxiliary electrode(s) will be closely adjacent to the said selected areas. Typically the auxiliary electrode may be spaced from the selected areas by a distance of 1 mm. to 10 mm., say 5 mm. It will be apparent to those skilled in the art that the particular distance will depend upon various considerations including the size of the selected area and of the auxiliary electrode. Thus where the selected area and auxiliary electrode are both small, it may be possible to attain the desired results by positioning the auxiliary electrode close to the selected area. Where the selected area is quite extensive, it may be desirable to space the auxiliary electrode a greater distance therefrom.

When electroplating according to this invention, the cathode piece may be placed within an appropriate elec-

trolyte bath containing one or more anodes. The anodes and cathodes may be energized by a direct current power supply. In practice of the invention, the auxiliary electrode may be energized by a polarizing power supply, the positive leg of which may be connected to the negative leg of the main power supply for the anode and cathode. The negative leg of the polarizing power supply may be connected to the auxiliary electrodes. The preferred polarizing power supply which may be employed in practice of this invention may be one characterized by a high internal resistance.

The energy output of the polarizing power supply will be such, with respect to the main power supply, that the selected areas of the cathode are maintained anodic to the auxiliary electrodes. Typically this may be effected, e.g. in the case of chromium plating, by maintaining a potential difference between the selected areas of the cathode and the auxiliary electrode of at least 2 volts, and preferably 3 to 5 volts in the case of chromium plating. In the case of nickel plating, this voltage may be e.g. 0.2-0.3 volt.

Thus a preferred embodiment of the apparatus by which the instant invention may be practiced may include, suspended in an electroplating bath, an anode (or anodes), a cathode having predetermined areas to be plated and selected areas to be stopped-off, an auxiliary electrode (or electrodes) suspended adjacent to each of the said selected areas of said cathode, a main power supply establishing a potential across the anode and the cathode, and a polarizing power supply establishing a potential between selected areas of the cathode and the auxiliary electrode, the positive terminal of the polarizing power supply being joined to the negative terminal of the main power supply.

Electroplating by the process of this invention may thus be effected by maintaining the anode, cathode, and auxiliary electrode in the noted bath for a predetermined time at desired conditions of temperature, current density, etc. During this time, the cathode may be electroplated and it will be found that the selected areas to be stopped-off in fact have received no deposit of plate.

In an illustrative embodiment of this invention as shown in the attached drawing, a plating solution 10 may be contained in vessel 11 which contains a cylindrical cathodic piece generally designated 12. The cathode piece 12 may contain predetermined areas 13 on the outer surface thereof which areas are to be electroplated. The cathode 12 may also contain selected areas 14 whereon plating is not desired. Solution 10 also contains therewithin anode(s) 15. Cathode 12 and anode(s) 15 may be electrically connected to power supply 16 through conductors 17 and 18.

This embodiment of the apparatus also includes auxiliary electrodes 19 which may be thin cylindrical rings spaced from selected areas 14, which in the instant embodiment may be threads on a pipe if the cathode 12 be a threaded pipe or rod. Auxiliary electrodes 19 may be connected to polarizing power supply 20 through conductor 21 which joins auxiliary electrodes 19 to the negative terminal of power supply 20. The positive terminal of polarizing power supply 20 may be joined to the negative terminal of power supply 16 through conductor 22. The polarizing power supply circuit may include voltmeter 23.

Main power supply 16 may for example be an appropriate direct current generator. The polarizing power supply 20 may preferably be one characterized by high internal impedance. Preferably the relationship between power supply 16 and polarizing power supply 20 may be such that during operation of the process, the voltage differential between selected areas 14 of cathode 12 and auxiliary electrode 19 may e.g. in the case of a chromium plating bath typically be at least about 2 volts, and typically 3 to 5 volts.

In one illustrative example using the apparatus of the drawing, cathode 12 may be a threaded steel pipe 19 cm.

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long and 3.9 cm. outside diameter. The threaded areas 14 were approximately 2.5 cm. wide. The auxiliary electrodes 19 each were cylindrical pieces of Type 1040 steel having an internal diameter of 4.3 cm. and an external diameter of 4.6 cm. The height (i.e. width) of each auxiliary electrode was 2.5 cm.—i.e., approximately the same as the width of the threads of selected areas 14 of cathode 12. The auxiliary electrodes 19 were each mounted on an appropriate support thereby maintaining them in position.

In practice of a specific embodiment of the process of this invention, the electrolyte bath 10 may (for use in chromium plating) contain 225 g./l. chromic acid and 2.25 g./l. of sulfate ion from sulfuric acid. Anodes 15 may be a lead-tin alloy and the cathode 12 may be a low carbon steel. The auxiliary electrodes 19 were of Type 1040 steel. The bath was maintained at 50° C. Electroplating was effected at current density of 31 a.s.d. for 60 minutes. The auxiliary electrodes 19 were maintained at a potential of 3 volts with respect to the selected areas 14 of the cathode, and 15 amperes of current passed between the auxiliary electrodes 19 and the selected areas 14.

After 60 minutes, it was found that the predetermined areas 13 had received a bright lustrous chromium deposit having a thickness of 30 microns. The selected areas 14 were found to be entirely free of any chromium deposit and were entirely free of any change.

In another illustrative embodiment of this invention, nickel plating may be effected in the apparatus of the drawing. The cathode 12 and the auxiliary electrodes 19 were identical to those set forth in the first illustrative embodiment supra. The anodes 15 were of nickel. The electrolyte bath 10 may be a Watts nickel bath having the following composition:

Component:	Amount g./l.
Nickel chloride -----	40
Nickel sulfate -----	300
Boric acid -----	35

Electroplating may be effected at current density of 2 a.s.d. for 30 minutes. The auxiliary electrodes 19 may be maintained at a potential of 0.2–0.3 volt cathodic with respect to the selected areas 14 of the cathode, and 2 amperes current may pass between the auxiliary electrodes 19 and the selected areas 14. After 30 minutes, it was found that the predetermined areas had received a good Watts nickel deposit, having a thickness of 16 microns. The selected areas 14 were found to be entirely free of any nickel deposit.

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It is a particular feature of this invention that it permits attainment of a highly uniform deposit of e.g. chromium from one end of the plate to the other end of the plate. The deposited plate is entirely free from any bead effect and is characterized by its uniformly smooth surface and particularly by the smooth transition between the plated area and the unplated area. This eliminates the need for any mechanical finishing after plating.

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 and variations as come within the scope of the appended claims.

What is claimed is:

1. The process for electroplating a plate metal from a bath onto a cathode having predetermined areas to be plated and selected areas to be stopped off which comprises placing an auxiliary electrode adjacent to said selected areas, said auxiliary electrode containing a thin coating of platinum sufficient to substantially inhibit electroplating of said auxiliary electrode, maintaining said selected areas anodic to said auxiliary electrode, and subjecting said cathode to plating current density whereby said metal is deposited on said predetermined areas and said selected areas remain stopped off.

2. Apparatus for electroplating which comprises a container for an electroplating bath, at least one anode suspended in said container, an auxiliary electrode adjacent to said anode, said auxiliary electrode containing a thin coating of platinum sufficient to substantially inhibit electroplating of said auxiliary electrode, a main power supply means for establishing a potential between said anode and a cathode suspended in said container, and means for maintaining selected areas of said cathode anodic to said auxiliary electrode.

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