PRODUCTION OF ELECTROLYTIC METAL

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Filed: Mar. 17, 1971
Appl. No.: 125,423

U.S. Cl. ...........................................204/12, 204/11, 204/281
Int. Cl. ...........................................C23b 7/02, B01k 1/00, C23b 7/00
Field of Search ...................................204/3, 4, 11, 12, 281; 106/1, 106/2

References Cited
UNITED STATES PATENTS
2,765,230 10/1956 Tinklenberg.................................204/11
2,773,816 12/1956 Wesley et al..............................204/281
3,434,938 3/1969 Van Sciver ..............................204/11
3,489,666 1/1970 Nordblom et al...........................204/281
3,577,330 5/1971 Knapp et al..............................204/10

OTHER PUBLICATIONS
T. R. Bates, Photosensitive Resists for Electroforming; Plating Magazine July 1965 pp. 673-676
G. R. Schaar, Electroformed Screens with Controlled Hole Size for Battery Plaques, Plating Feb 1968 pp. 130-137

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ABSTRACT
Metals such as nickel are electroformed upon a matrix or mandrel having an epoxy resist pattern thereon to provide foraminous or dividable electrodeposited metal separable from the matrix wherein the matrix is prepared by depositing from 2 to 30 microinches of standard chromium thereon and the desired resist pattern is applied to the chromium-plated surface in the form of a thermoset epoxy ink or paint containing dicyandiamide as a heat-curing agent and then heat curing the resist pattern to provide a repeatedly reuseable matrix.

12 Claims, No Drawings
PRODUCTION OF ELECTROLYTIC METAL

The electroforming art has struggled with the problem of providing foraminous or dividable deposits of nickel and other metals for many years. For example, electroforming provides an economical method for providing screening made of nickel, copper or other metals on a continuous basis. In such an operation, a matrix or mandrel having a pattern of non-conductive spots corresponding to the openings desired in the electroformed screen is prepared. During the course of the electrodeposition upon the matrix, metal is electrodeposited upon the conductive areas of the matrix but does not deposit upon the non-conductive spots, thus yielding a foraminous metal sheet when the electrodeposited metal is stripped from the matrix. When the mandrel or matrix is provide as a slowly rotating cylindrical cathode in an electroplating bath, a continuous screening of nickel or other metal can be provided. The preparation of such matrices or mandrels in the past has been expensive since it has been considered necessary, because of the strong tendency of the electrodeposited metal to pull the non-conductive material with it when the metal is stripped from the matrix, to provide a physical anchoring of the non-conductive material in the face of the matrix. A cheaper means for providing non-conductive areas upon the matrix or mandrel which would enable the electrodeposited metal to adhere strongly to the mandrel surface during electrodeposition and stripping of the electrodeposited metal would be of great assistance in this connection.

In another area; to wit, electrorefining, it has been considered for years desirable to be able to provide the electrorefined metal in a form which could be easily subdivided. Thus, absent a means for providing the electrorefined metal, such as nickel, in a form which could easily be divided, the only means for providing the electrorefined metal in physical forms smaller in dimension than that of the cathode upon which the metal was deposited was by the route of shearing the cathodes. Since many electrorefined metals, including particularly nickel and copper, are tough and relatively hard, the shearing operation was accomplished only at considerable expense, and resulting sharp edges formed upon the sheared pieces presented handling problems and were undesirable from the labor standpoint. Traditionally, nickel has been electrorefined by a method wherein thin metal starting sheets were first prepared, and metal was deposited in the electrorefining cell on both sides of the starting sheet to an appropriate thickness usually on the order of about three-eighths of an inch. The Prescott U.S. Pat. No. 2,392,614 which utilized a slotted starting sheet and the Wesley et al. U.S. Pat. No. 2,773,816 which utilized interconnecting lines of a resist material represent prior endeavors in the art to provide dividable electrorefined cathodes of copper and of nickel, respectively. These prior attempts were characterized by relatively high cost and by the fact that the divided product produced thereby still presented sharp edges and difficulties in separating the resulting cathode into component pieces. Other workers have recognized that dividable electrorefined metal could be provided by utilizing a flat mandrel of a metal such as stainless steel bearing upon the faces thereof an interconnecting pattern of resist lines. The electrodeposited metal produced upon such mandrels could be separated from the mandrel and divided along lines corresponding to the initial lines of resist applied upon the faces of the mandrel. In order to apply such a technique to commercial production in an electrorefinny on an economic basis, it was speedily discovered that it was essential to provide a mandrel which could be reused numerous times, e.g., 10 times or more, in the electrorefining bath without having to replace or repalce the lines of resist from the faces thereof. It was found, however, that under the conditions existing in the cathode of the electrorefining process, the materials which could be employed as the resist materials but broke down speedily with the result that it was necessary to repair or replace the resist material each time the mandrel was returned to the process for further plating. Thus, materials such as electropaters tape, rubber base and plastic paints and inks, etc., which had been used as stop-offs in electroplating racks and the like, were found to be inadequate to meet the severe demands of this service.

The present invention is directed to a means for providing highly resistive areas upon an electroplating matrix or mandrel for use in electroforming.

Broadly stated, the present invention is directed to a process for electrorefining metals, including nickel, cobalt and iron, upon a mandrel which may be made of stainless steel, titanium, aluminum, iron and nickel, etc., wherein the mandrel is prepared by chromium plating faces thereof, applying to the chromium plated faces a thermostetting epoxy ink containing dicyandiamide as a hardener in the desired pattern as, for example, silk screen printing, curing the ink or paint film by heating, and thereafter electrodepositing metal thereupon. As noted hereinbefore, the ink or paint film may be applied to any desired pattern and may, for example, form a continuous pattern of interconnecting lines or areas upon the face of the mandrel so as to define conductive areas having the desired shape and size for the plated shapes to be produced.

The chromium plating, which is essential in accordance with the invention, can be accomplished in any standard chromium plating bath. As is known, chromium plating baths are usually aqueous metallic solutions containing at least about 50 grams per liter (gpl) of chromic acid (CrO3) and a catalyst such as sulfuric acid, with the weight ratio of chromic acid to sulfuric acid being about 50:1 to about 250:1, e.g., 100:1. A satisfactory aqueous chromium plating bath, for purposes of the invention, contains about 250 gpl of chromic acid and 2.5 gpl of sulfuric acid. Chromium can be deposited upon the face of the mandrel at a cathode current density of about 80 to about 200 amperes per square foot with a bath temperature of about 100°F. to about 120°F. being employed. The chromium deposit may be from about 2 to about 30 micrometres in thickness. The chromium deposit may be left upon the exposed areas of the mandrel with beneficial effects in connection with the electroforming of relatively thin foraminous materials, e.g., screen, which usually are plated to a thickness range of about 0.0001 to about 0.001 inches. In such a case the epoxy ink or paint pattern would be discontinuous, e.g., a system of dots. When the electroforming is part of a nickel electrorefining operation and the mandrel material is stainless steel or titanium, the chromium deposit advantageously is removed from the exposed areas of the mandrel prior to electrefodeposition of metal thereon. This may be accomplished, for example, by anodic dissolution in an alkaline solution, e.g., sodium carbonate or sodium hydroxide water solution. As an example, an aqueous solution containing about 20 to about 50 gpl of sodium hydroxide may be employed and current may be passed from the mandrel as anode at a current density of about 10 to about 60 amperes per square foot. In this way, a mandrel can be produced on which adhesion of heavy deposits, e.g., at least about 1/4 inches thick of, for example, nickel, is facilitated.

Any of the standard acid, aqueous nickel electroplating or electrorefining baths, e.g., the sulfate-chloride (Waste) bath, the all-chloride bath, the sulfamate bath, the sulfate-sulfamate bath, etc., may be employed in carrying out the invention. These baths usually are buffered with boric acid and are operated within the pH range of about two to about four, at temperatures of about 110° to about 150°F. and at cathode current densities of about 20 to about 50 amperes per square foot (a.s.f.). The baths may contain usual brightening or leveling agents, e.g., hydrazonitrile in the amount of about 15 milligrams to about 75 milligrams per liter, and may contain agents to incorporate a small amount of sulfur in the nickel deposited, e.g., about 0.005 to about 0.025 grams per liter (gpl.) of sulfur or carbon and amount which will provide about 0.005 to about 0.025 percent of sulfur in the deposited nickel.

Alloy deposits may also be produced, e.g., nickel-cobalt alloy deposits, again using standard bath compositions for this purpose. Standard cobalt and iron plating solutions may also be used, as disclosed in Modern Electroplating, edited by F. A. Lowenheim, John Wiley and Sons, Inc., (1963).
A problem encountered in carrying out the invention in the production of electrolytic metal having substantial thickness, e.g., at least 0.25 inch, is that of lifting or separation of the electrolytic metal from the exposed metal mandrel surfaces when the stress level becomes excessive. The use of a small amount of sulfur co-deposited with the nickel provides a controlled stress relief in a nickel deposit produced from the sulfate-chloride bath. Thus, a sulfur content of about 0.01 percent to about 0.02 percent in electrolytic nickel, provided through the incorporation of about 0.01 percent to about 0.02 percent of sulfur dioxide in the electrolyte, will usually provide a stress level of preferably ±5000 pounds per square inch in the nickel. Such nickel is useful as nickel electroplating material because of its high chemical and electrochemical activity, as is discussed in the Renzoni et al. U.S. Pat. No. 3,437,571. When such nickel is deposited in an electroplating or electrorefining operation upon a stainless steel mandrel having a pickled surface, good adherence of the deposited nickel and of the resist film to the stainless steel surface is obtained. However, when it is desired to produce sulfur-free nickel in substantial thickness, from, e.g., the sulfate-chloride bath, the metal, e.g., stainless steel, mandrel must first be roughened by means of a sand blasting operation using grit at least as coarse as "No. 2", having an average particle size in excess of 200 microns.

In order to give those skilled in the art a better appreciation of the advantages of the invention, the following example is given. Ten type 304 stainless steel blanks, about 29 inches wide by 40 inches long by 0.125 inches thick and having a pickled finish were prepared by subjecting them to cathodic alkaline cleaning and water rinsing, and were then plated with about 10 micrometers of copper by passing current thereto for about 24 minutes at 1 ampere per square inch in a chromium plating bath containing 250 gpl chromic acid and 2.5 gpl sulfuric acid. The temperature of the chromium plating bath was 113°F. The chromium plated blanks were then hot water rinsed and dried. The dried blanks were then silk screen printed to define a pattern of uncoated, conductive circular areas about five-eighths inch in diameter in staggered rows with a minimum spacing of three-eighths inch between the circular areas using as a resist material an epoxy ink containing in parts, by weight of effective ingredients, about 12 parts of diglycidyl ether of bisphenol A (epoxy resin), about 7 parts of 20 weight percent titanium dioxide, 80 weight percent calcium carbonate pigment and about 1 part of dicyandiamide hardener. The silk screened blanks were then oven-cured at about 350°F. for about 40 minutes to set the epoxy resin. The chromium was removed from the exposed areas of the mandrels by exposing them as anode for about 10 minutes in an aqueous solution containing 45 gpl sodium hydroxide at an anode current density of 10 asf. The blanks were then plated in an electrorefining cell containing an aqueous sulfate-chloride nickel electrolyte to build upon on each face thereof a thickness of nickel of about three-eighths inch. The plating bath contained about 55 gpl nickel, 20 gpl sodium, 50 gpl chloride, 20 gpl boric acid, 85 gpl sulfate and 0.02 gpl sulfur dioxide. The plating process proceeded for about ten days and the nickel deposit contained about 0.025 percent sulfur. No adherence problem arose in plating. After plating, the blanks were removed from the tanks, and the nickel deposit in the form of circular segments was stripped from each face thereof. The blanks were returned for further plating without overhaul of the epoxy resin film pattern. The process was repeated about 10 times without overhaul of the epoxy film pattern being necessary.

In comparison to the successful results obtained when the stainless steel starting blanks were chromium plated prior to silk screen printing with the epoxy ink, it was found that films produced identical directly on the surface of the same stainless steel (without chromium plating) failed quickly with the result that the prepared blanks could not be reused without repair or replacement of the cured epoxy film. In this connection it is to be recognized that electrodeposited metal such as nickel will penetrate even microscopic pores in a stop-off film with resulting damage to the film when the deposit is stripped. This factor has made it extremely difficult to find any type of film forming pattern material which would resist the severe service encountered in exposure of the film to conditions existing at the cathode in an electroplating bath during operation. Thus, many types of inks and paints which yield a film which appears sound to the eye or even under the microscope fail rapidly in this service.

Not only is the chromium plating necessary to secure requisite adhesion of the epoxy film pattern to the cathode blank; but, further, it appears that only epoxy ink or paint formulations, wherein the epoxy resin is cured, hardened or "dried" by dicyandiamide, are satisfactory. These formulations are especially satisfactory for silk screen printing, since they are cured by heating at temperatures of at least about 350°F. and, hence, remain liquid in the silk screen printer even for times as long as a week or more. Ink formulations hardened by aliphatic or aromatic polyamines, anhydrides, etc., are not satisfactory.

The epoxy resin used in the ink formulation, which is a mixture of glycidyl ethers of bis-phenol, should itself have a viscosity in the range of about 400 to about 600 centipoises at 100°C since, as those skilled in the art know, viscosity of the resin is a useful indirect measure of the epoxy content. The pigment component of the ink performs a useful function in that pigmented films assist in inspection of the blanks for film damage. The pigment is preferably titanium dioxide, which may be extended with, for example, calcium carbonate. The pigment is not essential to the performance of the epoxy resist material. It is to be appreciated that the electrodeposited metal grows across the resist material during plating. Thus, in order to yield a deposit which is readily separable into segments, the minimum width of the resist areas should not be substantially less than the thickness of the electrodeposited metal to be plated. The ink may contain a small amount of colloidal silica ("Aerosil") to provide a thixotropic effect.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

1. In the electrorefining of nickel wherein nickel is electrodeposited from an acid aqueous sulfate-chloride nickel electrolyte upon a sheet-form cathode blank having interconnecting areas of non-conductive resist material applied to said blank to define conductive islands on the faces thereof and relatively heavy dividable nickel deposits separable from said cathode blank are formed thereon, the improvement which comprises producing repeatedly reusable stainless steel cathode blanks by chromium plating said cathode blank, applying a film of epoxy-base paint cured by means of dicyandiamide to the resulting chromium surface and heat-curting said paint film to form said interconnecting areas of resist, whereby said epoxy-base paint film adheres strongly to said chromium plated stainless steel during said electrodeposition process.

2. The process according to claim 1 wherein the chromium deposit is removed from the conductive islands prior to the electrodoposition of nickel thereon.

3. The process according to claim 1 wherein the chromium plate has a thickness of about 2 to about 30 micraiches.

4. The process according to claim 1 wherein the pattern of interconnecting areas of resist is applied to said stainless steel blanks by silk screen printing.

5. The process according to claim 1 wherein the epoxy paint comprises in parts by weight of effective ingredients, about 12 parts of epoxy resin having a viscosity as 38°C of about 400 to 600 centipoises, up to about seven parts of pigment and one part of dicyandiamide.

6. The process according to claim 5 wherein the pigment is titanium dioxide with from 0 to 80 percent calcium carbonate.
7. The process according to claim 1 wherein the conductive islands are substantially circular and are applied in staggered rows.

8. The process according to claim 1 wherein the stainless steel cathode blank has a pickled surface and the nickel deposit contains about 0.005 percent to about 0.025 percent sulfur.

9. The process according to claim 8 wherein said nickel deposit contains about 0.01 percent to about 0.02 percent sulfur.

10. The process according to claim 1 wherein the stainless steel cathode blank has a sandblasted surface and the nickel deposit is essentially sulfur-free.

11. In the electroforming of nickel upon a stainless steel matrix having on the surface thereof a pattern of resist material, the improvement for providing a strongly adherent pattern of said resist material upon said matrix surface which comprises chromium plating said surface, applying to said chromium-plated surface a resist pattern of an epoxy-base ink containing dicyandiamide as a hardener, heat-curing said resist ink pattern and electrodepositing nickel upon said matrix bearing said cured ink pattern whereby said matrix may be employed repeatedly without damage to said cured resist pattern.

12. In the electrodeposition of a metal from the group consisting of nickel, cobalt and iron from an acid aqueous electrolyte upon a sheet-form cathode blank having a continuous pattern of non-conductive resist material applied to said blank to define conductive islands on the faces thereof and relatively heavy dividable metal deposits separable from said cathode blank are formed thereon, the improvement which comprises producing repeatedly reusable cathode blanks made of a metal from the group consisting of stainless steel, titanium, aluminum, iron and nickel by chromium plating said cathode blank, applying a film of epoxy-base paint cured by means of dicyandiamide to the resulting chromium surface and heating said paint film to form said interconnecting lines of resist, whereby said epoxy-base paint film adheres strongly to said chromium plated metal cathode blank during said electrodeposition process.

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