March 2, 1971 C. B. YATES 3,567,595

ELECTROLYTIC PLATING METHOD

Filed Sept. 25, 1967 3 Sheets-Sheet 1

Fig. 1.

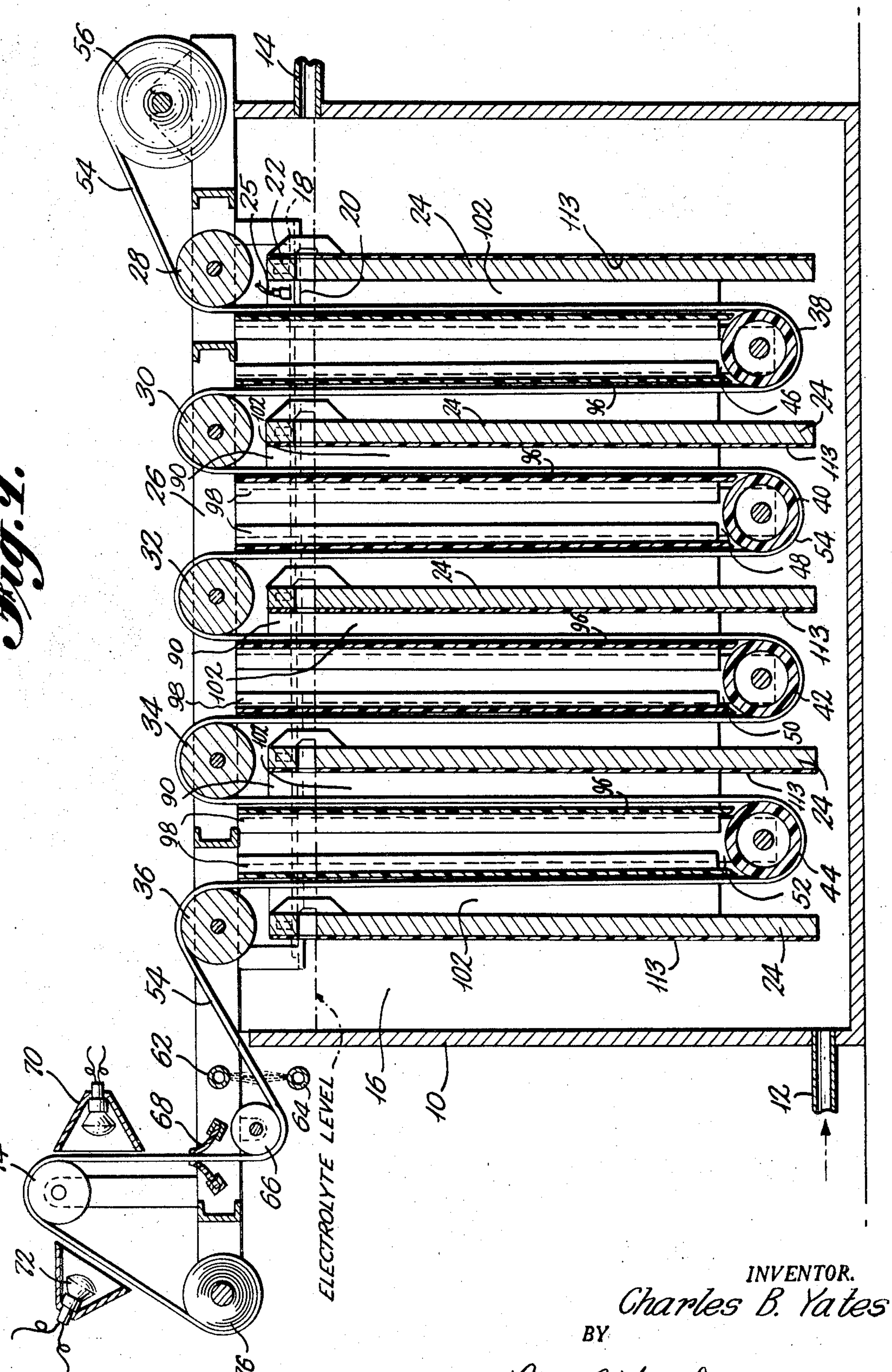

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Fig. 2.

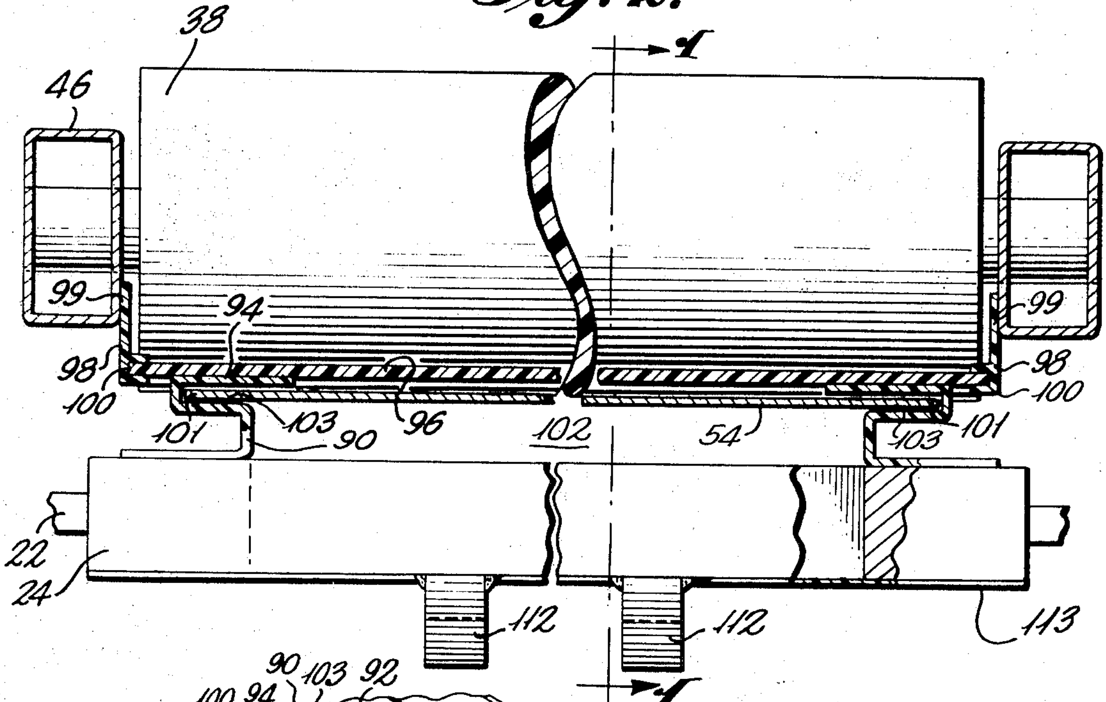

Fig. 3.

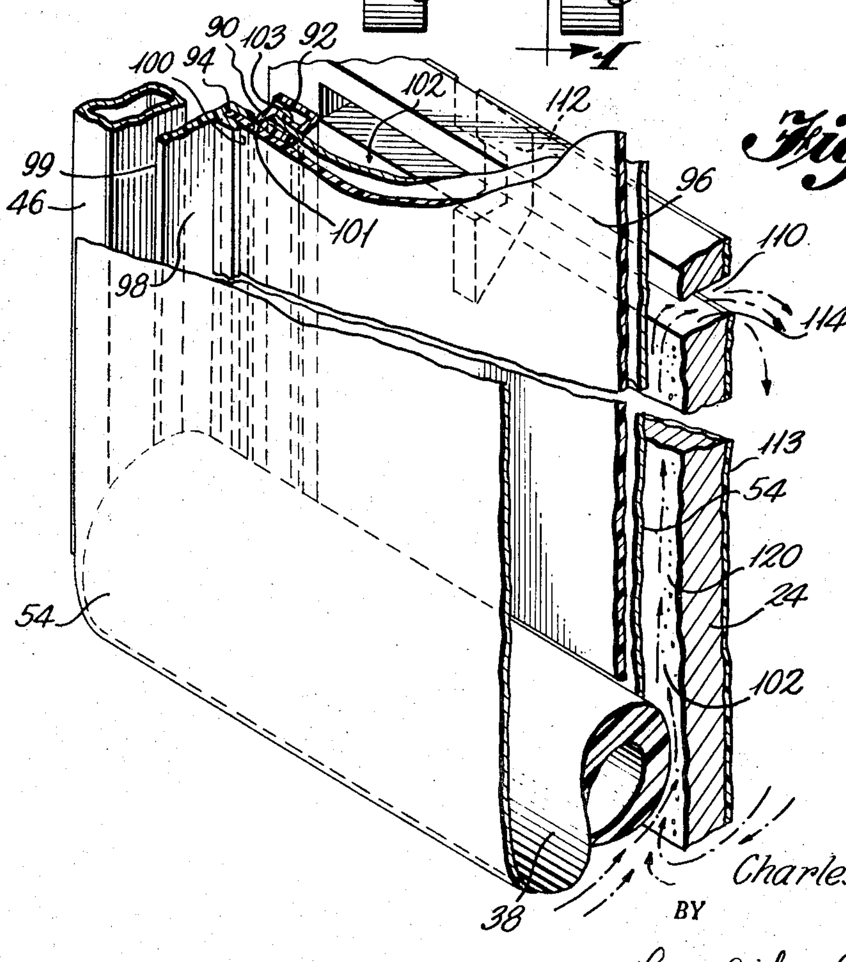

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Fig. 4.

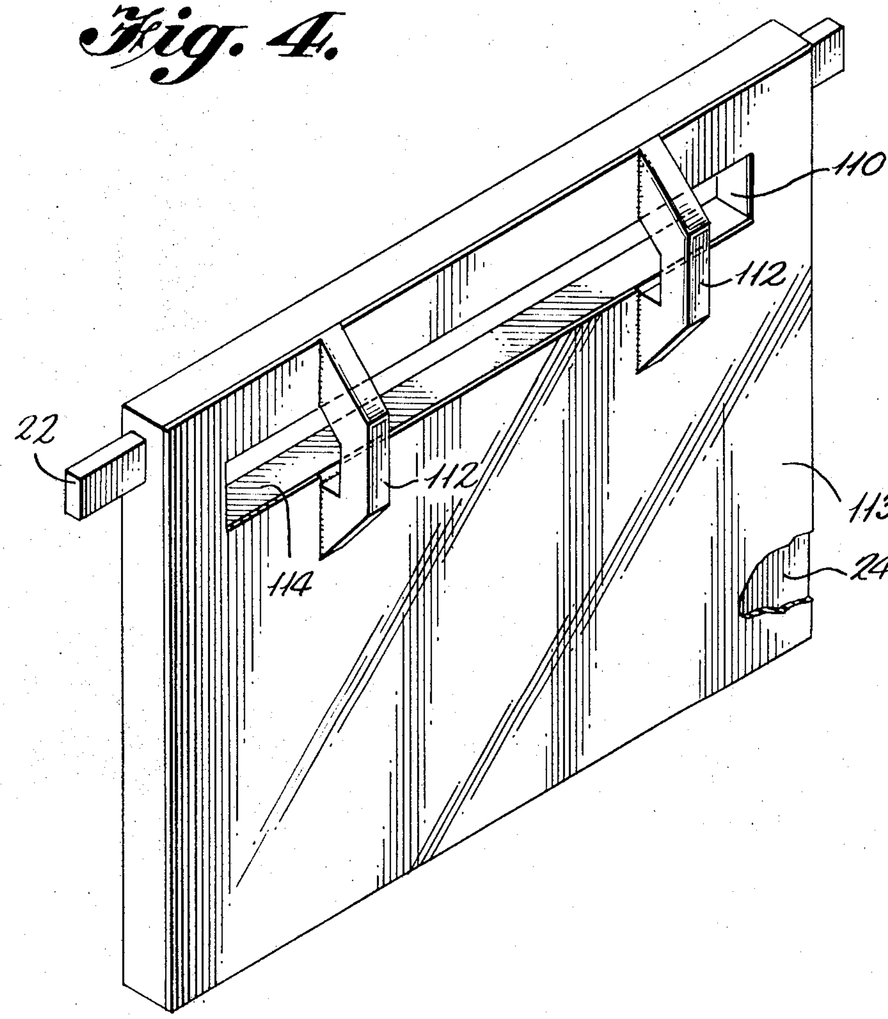
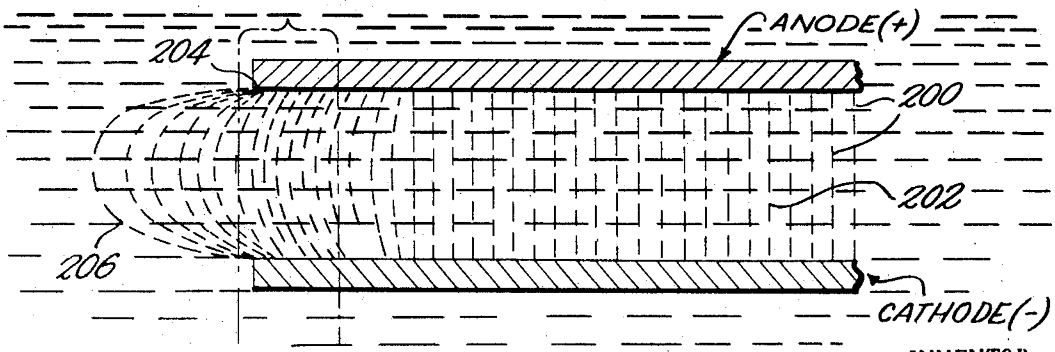


Fig. 5.



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ELECTROLYTIC PLATING METHOD

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U.S. Cl. 204—28 9 Claims

ABSTRACT OF THE DISCLOSURE

A method of improving the electroplating of a metal onto the surface of a cathodic strip of metal which is moved in the electrolyte in proximity to the surface of an anode, said method involving the creation of a substantially uniform upward flow of electrolyte across the surface of said strip of metal using gas evolved between the anode and said strip of metal as the driving force for a pumping system to create an air lift effect. Apparatus for carrying out said method.

This invention relates to an electrolytic process and the apparatus used therein and more particularly to a process and apparatus for continuously electroplating a moving strip of metal.

Electroplating techniques are known in which a continuously moving metallic sheet is moved in serpentine fashion into and out of an electrolyte between successive planar anodes vertically arranged in parallelism with one another. By rendering the metallic sheet cathodic, metal is electrodeposited in the sheet as it traverses the electrolyte. A system of this type is illustrated and described in copending application Ser. No. 421,048, filed Dec. 24, 1964 and now abandoned.

In such an electroplating process, it is highly desirable that the metallic deposit be of a very high degree of uniformity of thickness. Two problems are encountered in conventional methods which result in variations in coating thicknesses which are inadequate. First, electrical current which flows from the cathode to the anode in an electroplating process often leaves the desired plating surface in a non-uniform manner, which results in uneven current distribution and plating. In addition, the weight of the deposited material often varies due to changes in the deposition current efficiency resulting from an ionic imbalance in the electrolyte bath. This ionic imbalance has been found to occur because of variations in degree in flow and agitation in the electrolytic bath during the deposition process.

Problems such as the foregoing become particularly troublesome in certain electrolytic processes such as, for example, one involving the electrodeposition of chromium on a moving metallic sheet. For some electrolytic systems, establishing a uniform current distribution is adequate to obtain an adequate electrodeposit. In chrome plating, however, this is not enough. More specifically, the common chrome plating baths in commercial use have current efficiencies between 20 and 35% and the efficiency has been shown to be related to a wide collection of bath variables such as chromate to sulfate ratio, foreign metal contamination, temperature, agitation, degree of physical electrolye exchange from cathode to anode, and so forth. In order to achieve a uniform chrome deposit, it is necessary for the electrolyte bath to behave uniformly with respect to current efficiencies of deposition at different parts of the cathode. Thus, the uniformity of the flow and agitation pattern in the electrolyte is of very great importance in achieving a uniform thickness of chrome deposit.

The importance of a uniform chrome layer takes on added significance when considering the use of a product such as chrome plated copper foil as a bimetallic lithographic or offset plate. In processing such a plate, starting with a chrome plated copper sheet, part of the chrome surface is masked with a photosensitive polymer leaving the areas of chrome which it is desired to remove exposed, such that they may be attacked by an etchant. As the chrome is attacked in the etching step, there is a tendency for the etchant to attack sideways as well as vertically causing the area of the base copper which is finally exposed to be somewhat larger than the area of chrome originally exposed. This problem is called "dot growth," its name coming from the manifestation of the effect in the etching of half tone dots where the eye has been shown to be sensitive to infinitesimal variations in dot diameter which in turn cause variations in the shading or color density of an area.

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In developing transparent positives for use in bimetal plate making, the camera attendant normally adjusts the dot size of the transparency to allow for a given degree of dot growth. The problem arises in that the degree of dot growth is a direct function of the chrome thickness, and chrome plates made in the conventional sheet by sheet manner suffer from all of the undesirable edge effects and non-uniform flow and agitation effects of a still bath. Thus, the printer in using such plates is forced to accept an undesirable degree of variation in dot growth which, in multicolor work, seriously diminishes the quality of the result. In this particular usage, uniformity of chrome thickness assumes a unique degree of importance not often necessary in other sorts of chrome plating.

The present invention provides a process and apparatus for continuously electroplating a sheet of metal foil wherein the above-mentioned disadvantages are eliminated. An even deposition of the electrodeposited layer is obtained by utilizing a novel electrically insulating shield and anode barrier arrangement in the plating tank which permits the control of the flow and agitation of the electrolytic bath during deposition.

It is accordingly a primary object of the present invention to provide a novel continuous electroplating process which is extremely effective to form high quality, uniformly thick, metallic electrodeposits on a sheet of base metal.

It is a further object of the present invention to provide a novel electroplating process and apparatus for carrying out such process whereby a sheet of metal may be continuously electroplated in which the electrolyte circulation is controlled by a unique anode and insulating barrier construction.

It is still another important object of the present invention to provide a novel anode structure which makes possible the obtaining of electrodeposits which are extremely uniform in thickness.

These and further objects and advantages of the present invention will become more apparent through reference to the following description and appended claims, as well as to the accompanying drawings wherein:

FIG. 1 illustrates a longitudinal section of an electrolytic apparatus in accordance with the present invention taken along line 1—1 in FIG. 2;

FIG. 2 is a plan view partially in section of a portion of the apparatus in FIG. 1;

FIG. 3 is a fragmentary sectional perspective view of a portion of the electrolytic apparatus of FIG. 1;

FIG. 4 is a perspective view of the anode used in the present invention; and

FIG. 5 illustrates in schematic form part of a plating bath in the area near the edge of an anode and a cathode.

As previously indicated, the novel method and apparatus of the present invention are applicable to the electroplating of any metal on a base metal where uniformity of thickness of the electrodeposit is desired, such as copper on copper, chrome on copper, copper on steel, or the like. Since such novel method and apparatus are particularly advantageous in chrome electroplating systems, however, the ensuing description will be couched in terms of the electroplating of chrome on a continuous strip of copper, though the broad essence of the invention is not to be deemed as being so restricted.

The electroplating apparatus illustrated in FIG. 1 comprises a tank **10** containing an electrolyte inlet **12** and outlet **14** for entrance and withdrawal of electrolyte **16** from the tank **10**. A positive bus bar **18** is secured to one longitudinal edge of the tank **10** by means of an insulating strip **20**. Supported on the bus bar **18** and insulating strip **20** by means of copper bars **22** are a plurality of anodes **24**. These anodes **24** are shown in the form of thick planar lead plates, whose physical configuration forms an important feature of the present invention, as hereinbelow described. A terminal lead **25**, adapted to be connected to the positive terminal of a power source (not shown), is connected to the bus bar **18**. A support frame **26** is mounted on the tank **10**. In order to guide a sheet of copper **54** to be plated, a series of upper electrically conductive idler rollers identified by the numbers **28**, **30**, **32**, **34** and **36** are mounted on and are in electrical contact with the support frame **26**, and a series of polyvinyl chloride idler rolls **38**, **40**, **42** and **44** are rotatably mounted on stainless steel bars **46**, **48**, **50** and **52**, which in turn are connected to the supporting frame **26** at their upper ends. By virtue of the electrical contact between rollers **28**, **30**, **32**, **34** and **36** and support frame **26**, and by connecting the latter to the negative terminal of a power source (not shown), copper sheet **54** may be rendered cathodic.

The continuous sheet of copper **54** which is to be electroplated is shown fed from a supply spool **56** mounted on the support frame **26**, over the first upper idler **36** and into the electrolytic bath **16**. The continuous sheet **54** is guided into and out of the electrolyte **16** in serpentine fashion by means of the remaining idler rollers **38**, **40**, **42** and **44** at the bottom of the tank **10** and the upper idler rollers **28**, **30**, **32** and **34**. As the plated sheet **54** emerges from the electrolytic tank **10** it passes by a pair of nozzle elements **62** and **64** which are connected to a source of wash solution (not shown) to permit the sheet **54** to be spray washed on both sides. The plated sheet metal then is fed across idler roller **66**, past a squeegee device **68** which removes any excess material, past a pair of infrared lamps **70** and **72** to dry the plated material, onto an additional idler roller **74** and finally to the take-up roll **76** which is provided with a suitable drive mechanism (not shown) which provides the necessary force to draw the sheet of copper **54** through the system.

The system thus far broadly described is conventional. Details of the essence of the present invention are shown specifically in FIGS. 2–4. FIG. 2 illustrates a section of the electroplating system as viewed from the top. This section includes an anode **24**, a cathode (which is the copper sheet **54** to be plated), a bottom idler roll **38** and a bottom roll support tube **46**.

Secured to each side edge of anode **24** at **92** is one leg of a reverse S-shaped barrier **90**, which is preferably constructed of a non-conductive material such as polyvinyl chloride. The other leg of each barrier **90** is secured at **94** to one edge of a back shield **96** which is preferably constructed of polyvinyl chloride or similar non-conductive material. Back shield **96** is mounted by means of non-conductive brackets **98** (preferably made of polyvinyl chloride) each of which has a slot **100** which engages an edge of back shield **96**. Each of brackets **98** is, in turn, secured to a support tube **46** at **99**. As shown in FIG. 2, the edges **101** of copper sheet **54** are positioned within a channel **103** formed within barrier **90** but are not secured to barrier **90** so that movement of sheet **54** will not be obstructed.

As will be readily seen from the drawings, by virtue of the presence of barriers **90**, the electrolyte between each anode **24** and the portion of sheet **54** which is parallel to and adjacent the planar face of the anode is effectively segregated from the remainder of the electrolyte in tank **10** to form channels **102** which are confined by four walls (barriers **90**, an anode **24** and sheet **54**) but which are open in a slot of uniform width at the bottom and open at the top. By virtue of the parallelism between anodes **24** and the adjacent portions of sheet **54**, confined channels **102** each have a substantially constant cross-section from the bottom to the top of anodes **24**. As will be seen hereafter, the establishment of these confined channels **102** forms an essential aspect of the present invention.

Details of anodes **24** are shown in FIG. 4. Each anode **24** is comprised of a slab of conductive material (preferably lead in a system in which chrome is plated on a copper sheet) and is provided with a pair of conductive projections **22** (which may appropriately comprise the ends of a single copper bar) which are used to mount anode **24** on bus bar **18** so as to establish an electrical connection between the power source and the anodes. Positioned near the top of each anode **24** but slightly below projections **22** is a longitudinal and horizontally extending slot **110**. Reinforcing bars **112** mounted over bracket slot **110** provide structural strength to the anode. Secured to one face of each anode **24** by conventional means (not shown) is a non-conductive sheet **113**, which may appropriately be made of polyethylene.

The operation of the system of the present invention may be described as follows. A sheet of metal **54** of suitable width is fed from supply roll **56** into and out of the electrolyte solution **16** over the upper idler rollers **28**, **30**, **32**, **34** and **36** and the lower rollers **38**, **40**, **42** and **44**, past idler rollers **66** and **74** to the take-up reel **76**. Upon energizing the system, the motor driven take-up reel **76** drives the sheet of metal **54** at a desired speed through the electrolytic bath **16** while a positive voltage is applied to the anodes **24** and a negative voltage to the metal sheet **54** acting as a cathode.

In order to achieve uniform deposition of the chrome layer on the copper sheet **54**, it is essential that a uniform flow distribution of electrolyte material between the cathode and anode be achieved. Because of gas generation which takes place at the anode interface (generally shown by the bubbles at **120** in FIG. 3), the channel **102** between the anode **24** and the copper sheet **54** is filled with a foamy solution whose average density is less than the average density of the remainder of electrolyte **16**. This causes a Pohle air lift effect which carries the liquid electrolyte **16** up towards the top of anodes **24**. By mounting anodes **24** so that the lower edge **114** of slot **110** is substantially level with the surface of the electrolyte **16**, the foamy electrolyte is caused to rise up in channel **102** and to flow through slot **110** as shown in FIG. 3. The result is that a circulation pattern is formed from the bottom to the top of channel **102** and through slot **110** of anode **24**.

Because this circulation pattern is confined within channel **102**, the pumping action of the generated gas causes the whole electrolyte body **16** to move upwardly at substantially the same velocity across the width of the metal sheet **54**, and to flow out over the anode **24** through the slot **110** at a uniform rate across the entire width of the anode **24**. This creates a uniform flow pattern in the desired direction, with no eddies and no still zones. All of the agitation and pumping effects of the generated gas occur in the same manner and cause the same results across the entire width of the plating area of the metal sheet **54** because the flow pattern is entirely unidirectional and there is no factor or effect which would tend to disturb this uniformity. The result is uniform thickness of deposit across the width of sheet **54**.

By virtue of the unique arrangement described above, the nature of the electrodeposit on the metal sheet can be readily modified by control of electrolyte circulation within confined channel **102**. Since the electrolyte circulation within channel **102** is directly related to the amount of electrolyte which is caused to flow through slots **110** of anodes **24** as a result of the gassing of the electrolyte as aforesaid, the electrolyte circulation can be modified by adjustment of the position of slots **110** relative to the electrolyte surface. By raising anodes **24** above the level of the electrolyte solution **16**, the flow of electrolyte over the anode slot **110** may be impeded somewhat. By bringing the anode **24** down below the level of the electrolyte solution **16**, it is easier for the electrolyte to be lifted by the gassing effect and to pass through the slot **110**, thereby increasing electrolyte flow. Thus, the flow rate in the plating area can be readily adjusted by adjusting the height of the anode **24**.

The exact position of the anode **24** must be determined for each specific application and depends on a number of variables including the distance between the cathode and anode, the materials utilized, the electrolyte solution, the rate of movement of the sheet of material to be plated and the thickness of the plating desired. If the anode is placed too high above the level of the electrolyte solution **16**, there will not be a sufficient flow rate and the electrolyte will become depleted in terms of its chromate content (in systems in which chrome plating is taking place), which will result in a loss of current efficiency and produce poor electroplating. If the anode **24** is placed too far below the level of the electrolyte solution **16** there will be virtually a still flow and the gasses will come up and simply bubble out of the electrolyte and not cause the desired lifting effect of the electrolyte across slots **110** of the anodes **24**.

In the preferred embodiment, the anode **24** has been shown with a slot **110** through which the electrolyte solution **16** flows, with separate projections **22** being provided above the lower edge **114** of slot **110** for mounting of the anodes. This particular construction facilitates the handling and mounting of the anode **24** and eliminates the necessity for sealing of the tank **10** at the points at which projections **22** come in contact with the supporting tank portion. While this arrangement is thus highly advantageous, the broad advantages of the present invention may still be achieved through the use of an anode without a slot by mounting such anode with its upper edge substantially level with the electrolyte surface. In such case, the upper edge of the anode performs the function of the lower edge **114** of slot **110**. As will be apparent, this arrangement requires that special precautions be taken to seal the tank at the points at which the anodes are mounted.

As will be apparent from the preceding description, the arrangement of the present invention is not only effective to establish uniform electrolyte circulation patterns between the anodes and adjacent moving cathodic metallic sheets (resulting in extremely uniform electrodeposits) but provides a significant secondary advantage. This secondary advantage results from the use of barriers **90** and their associated back shields **96** and can best be explained by reference to FIG. 5, which illustrates schematically current flow between a cathode and anode in an electrolyte both with no edge shield (such as barrier **90**) being present. In FIG. 5, the path of the current across the bath is represented by dotted lines **200** whose spacing indicates the current density across the electrolyte. In the right-hand area **202** of the sketch, where vast continuous areas of anode and cathode are exposed to one another at a uniform spacing, a uniform current density exists in the electrolyte assuming that the resistivity of the electrolyte is the same throughout its volume. In the area of the edge **204** of the sheet, the current will proceed directly across the electrolyte in the same manner and with the same density as in the right-hand area, but in addition to that current, the volume of the electrolyte to the left of the edge not directly between the anode and cathode is also capable of conducting current, and additional current will leave the anode in the area near the edge to take advantage of the conductivity of this extra volume of electrolyte. This extra flow of current is represented in FIG. 5 as dotted lines **206** extending well out into the side body of electrolyte. The conducting path may be somewhat longer, and as a result the actual current density across the electrolyte will fall off dramatically as one moves away from the anode edge to the left into the electrolyte volume, but the net effect as far as the cathode is concerned is a considerably higher total amount of current discharged at that edge, and consequently a thicker deposit.

In order not to confuse separate effects, the current lines which would normally emanate from the back of the anode (which is also at a potential relative to the cathode and the electrolyte, and which would also inevitably be the source of additional current) have not been shown in FIG. 5. This additional current, due to the greater exposed anode area which is often assumed to be the sole cause of edge build-up, is really only one of several contributing factors. For example, if the anode were insulated on its back and along its edges, entirely masking all of its surface other than that facing the cathode, there would still be a considerable edge build-up due to the greater volume of electrolyte available for carrying current near the edges of the electrodes.

In the system of the present invention, barriers **90** cut off all extraneous current paths immediately before the edges of the moving cathodic sheet **54**, so that current flow is not permitted to loop out into the side body of electrolyte. Except for a very narrow band of no more than 1–2 cm. in width, therefore, the edges of the sheet will see no more current flow than the center of the sheet. In addition, the back shields **96** will serve as a rear current barrier to prevent electrodeposition on the rear surface of sheet **54**. These functions are, as indicated, performed in addition to the primary function of establishing uniform electrolyte circulation patterns in conjunction with the unique anode of the present invention.

As previously indicated, each of anodes **24** is provided with a non-conductive sheet **113** on one of its faces. This non-conductive sheet has the effect of making each anode a one-sided anode so as to avoid gas evolution on both sides of the anodes. Unless this were done, the air lift effect on one side of a given anode would cancel out that on the reverse side and the advantages of the present invention would not be obtained. A similar effect could be obtained from placing two non-insulated anodes back-to-back in order to create a still volume of electrolyte between them.

The operating conditions employed in the carrying out of the process of the present invention will vary through wide limits depending on a number of variables including but not restricted to the nature of the base metal as well as plating metal, the thickness of the base metal, the thckness, smoothness and uniformity of the plating metal which is desired, the speed of movement of the base metal sheet throughout the electrolyte, and so forth. Those skilled in the art will have no difficulty adapting the proper conditions of the present invention to the production of a particular bimetallic product.

By way of example of the practice of the present invention, a matte chrome surface may be electrodeposited on a moving copper sheet approximately 60 inches wide using an electrolyte approximately as follows:

Bath composition:	Grams per liter
Chromic acid	200
Sulfuric acid	2

Utilizing the above electrolyte, the following approximate operating conditions may be employed:

Temperature—20–29° C. (preferably 25° C.)
Cathode current density—400 amps per square foot
Average tank voltage—6–8 volts

Anode-cathode spacing—¾ inch
Sheet speed—8 inches per minute
Bath time—2–4 minutes

Under the operating conditions set forth above, the thickness of a chrome plating on a copper sheet 5 mils thick will be approximately 2 microns.

The circulation of the electrolyte within the tank (other than that provided by the novel barrier-anode arrangement previously described) need not exceed more than 2 or 3 gallons per minute. This flow is sufficient to keep the electrolyte from being depleted but does not affect the flow characteristics caused by the Pohle air lift effect described above.

By means of the novel process and apparatus of the present invention, metal sheets can be produced having a continuously electrodeposited coating the thickness of which is extremely uniform across the entire width of the sheet. For example, while prior art techniques often result in coating thickness variations across the width of the sheet which vary 100% or more, the present invention can reduce this thickness variation figure to 50% and even to 10–30% and less.

The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The present embodiment and processes are therefore to be considered in all aspects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

What is claimed is:

1. In a process for electroplating a metal from an electrolyte solution onto the surface of an elongated strip of metal in which said strip of metal is in contact with an electrically conductive surface rendering the strip of metal cathodic in the electrolytic circuit, said strip of metal being moved through the electrolyte in proximity to at least one anode immersed in said electrolyte, said anode causing the evolution of gas in the electrolyte between said moving strip of metal and the side of the anode facing said strip of metal, the improvement comprising: creating substantially uniform upward flow of electrolyte past the surface of and substantially throughout the width of said strip of metal using said evolved gas as the driving force for a pumping system to create an air lift effect.

2. A process as defined in claim **1** wherein said air lift effect is of the Pohle type.

3. A process as defined in claim **1** wherein said substantially uniform upward flow of electrolyte is created by confining the electrolyte between said strip of metal and said anode to prevent the migration of electrolyte transversely across the edges of said strip; and maintaining the relative positions of the electrolyte surface and the anode

so that electrolyte is caused by the gas evolution to circulate up over a portion of the anode adjacent said electrolyte surface so as to obtain a substantially uniform circulation pattern within said confined body of electrolyte.

4. A process as defined in claim **3** wherein said electrolyte is confined by positioning a non-conductive barrier at each edge of said strip of metal and extending between said strip of metal and said anode.

5. A process as defined in claim **3** wherein said anode is mounted so that an exposed upper peripheral surface is positioned substantially level with the surface of the electrolyte.

6. A process as defined in claim **3** wherein a plurality of substantially vertically arranged, substantially planar anodes are immersed in said electrolyte and wherein said strip of metal is moved through said electrolyte in serpentine fashion so as to travel alternatively upwards and downwards between successively arranged anodes.

7. A process as defined in claim **3** wherein said confined body of electrolyte between said strip of metal and said anode has a substantially constant cross-section in a direction parallel to the direction of movement of said strip of metal.

8. A process as defined in claim **3** wherein said metal to be electroplated is chromium.

9. A process as defined in claim **3** wherein said anode is mounted so that an exposed upper peripheral surface is positioned substantially level with the surface of the electrolyte and wherein a plurality of substantially vertically arranged, substantially planar anodes are immersed in said electrolyte; wherein said strip of metal is moved through said electrolyte in serpentine fashion so as to travel alternatively upwards and downwards between successively arranged anodes; and wherein said confined body of electrolyte between said strip of metal and said anode has a substantially constant cross-section in a direction parallel to the direction of movement of said strip of metal.

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U.S. Cl. X.R.

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