May 3, 1966 G. HERMANN 3,249,520

PROCESS OF PROVIDING AN ELECTROLYTIC DEPOSIT ON A FACE OF A WORKPIECE

Filed Feb. 15, 1962

3 Sheets-Sheet 1

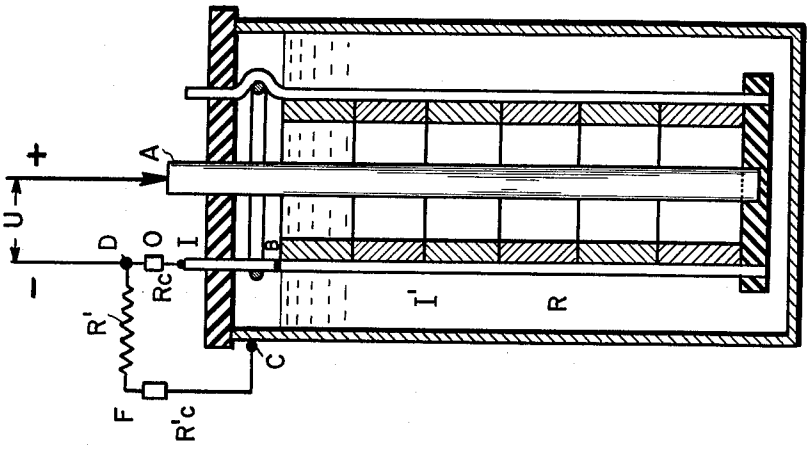

Fig. 3

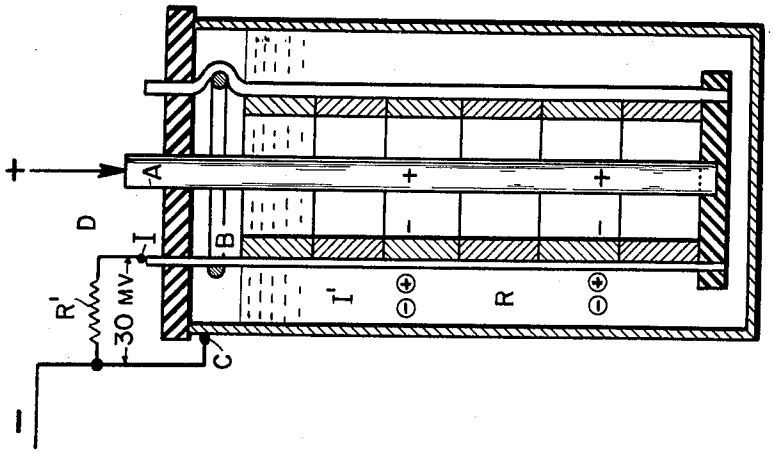

Fig. 2

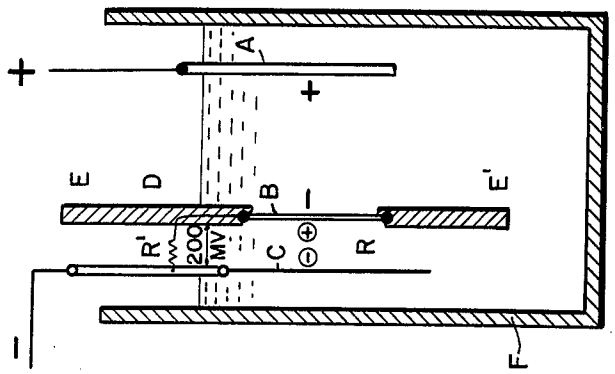

Fig. 1

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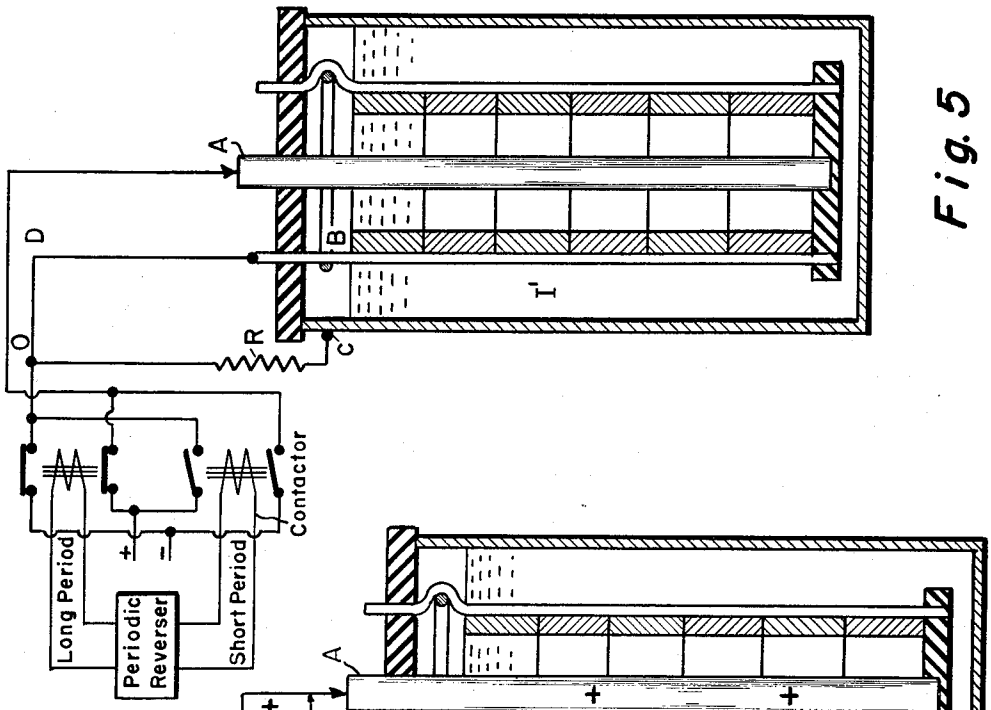

Fig. 5

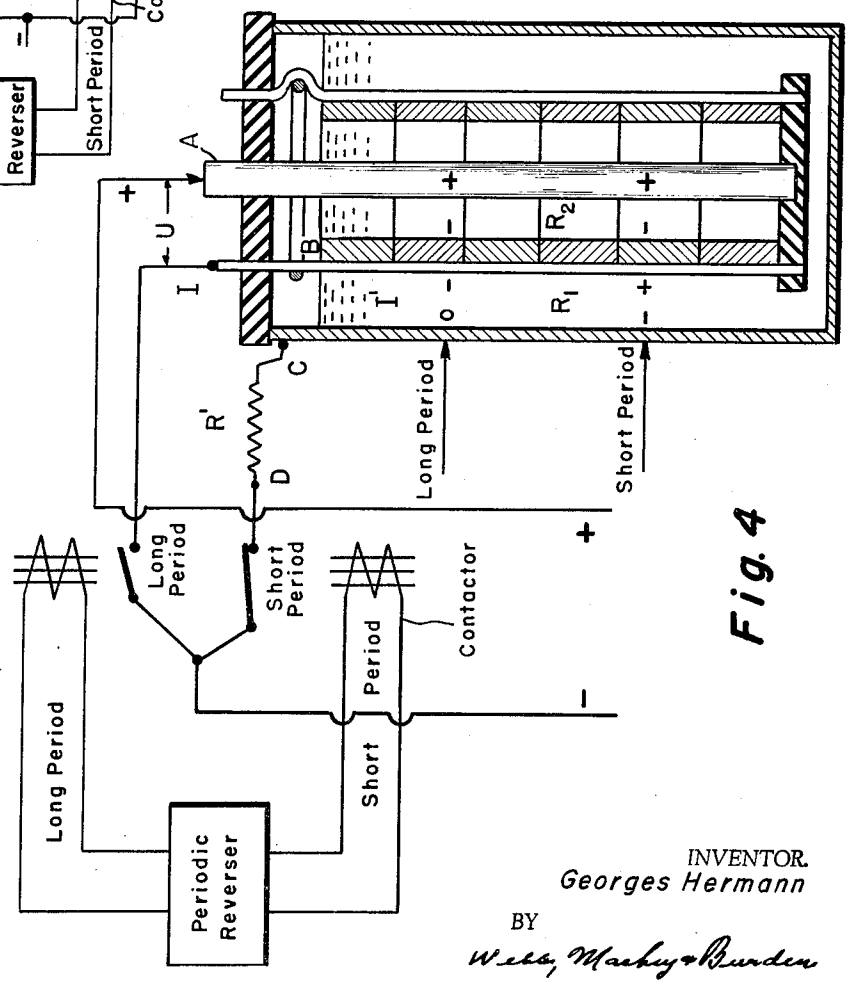

Fig. 4

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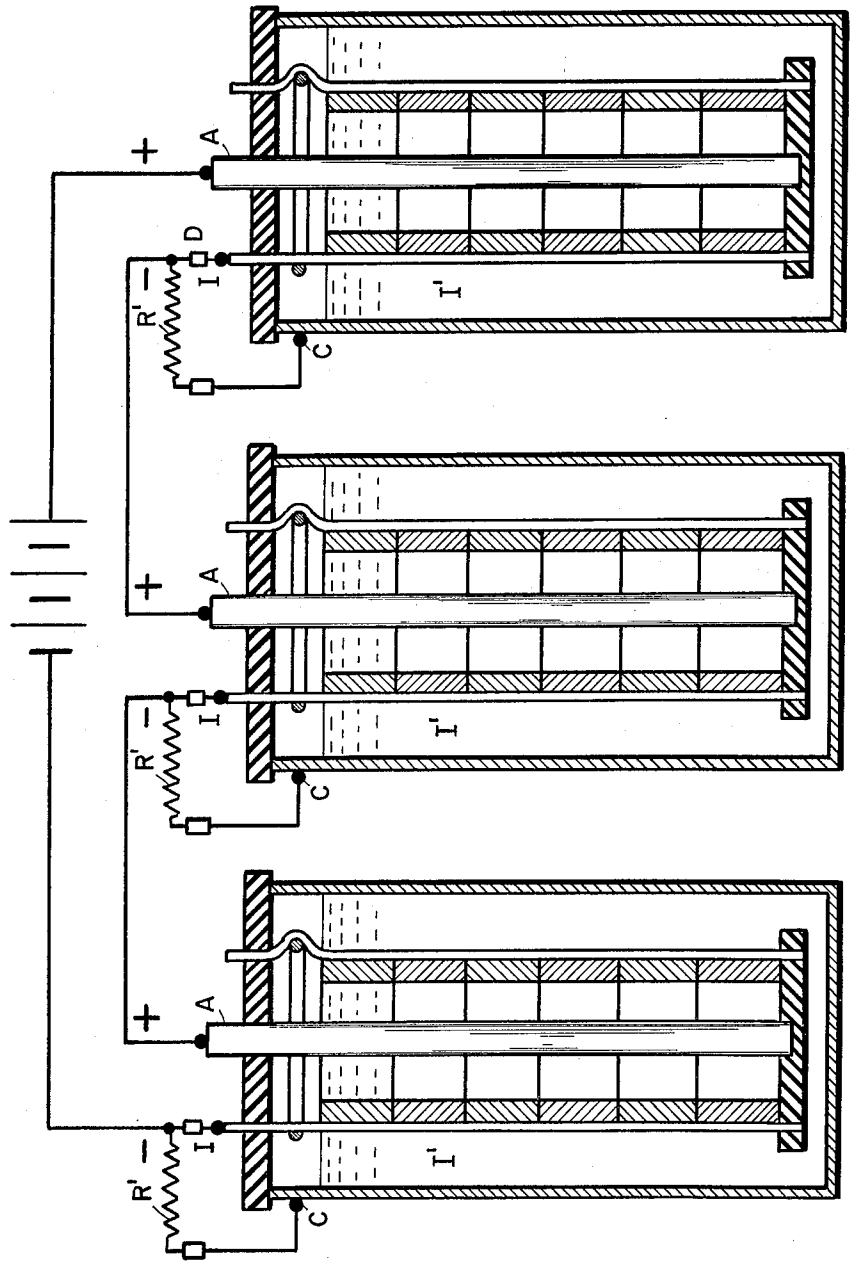

Fig. 6

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PROCESS OF PROVIDING AN ELECTROLYTIC DEPOSIT ON A FACE OF A WORKPIECE

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3 Claims. (Cl. 204—15)

This invention relates to a process of producing electrolytic depositions on a workpiece, such as a sheet, plate or cylinder and more particularly to effecting the deposition on part only, such as one face, of the workpiece.

In known electrolytic deposition processes for effecting the deposition on one face of the workpiece, the face which is to remain free of deposition is protected by means of varnish or of an insulating paste having a base, for example, of rubber, vinylic resin, or polyvinyl chloride. Such known processes, however, suffer from many drawbacks including long, delicate and troubesome preparations and poor adherence or destruction of the depositions on the workpiece in hot electrolytes having a high pH value, usually a pH value of 7 or higher. It is difficult when electrolytically plating bearings, for example, to protect the back of the pieces, especially if they are provided with orifices such as lubrication orifices or ducts.

The main object of the present invention is to provide an electrolytic deposition process by which the electrolytic depositions can be obtained on part of the surface, e.g., one face only of the workpiece.

According to the present invention, a process of providing an electorlytic deposit on a part of the surface of a workpiece, comprises disposing the workpiece as a cathode in the electrolyte of an electrolytic cell between the anode of the cell and a secondary or false cathode with the face of the workpiece on which the deposit is to be effected directed towards the anode, and applying an electric potential across the cell so that the electric potential difference between the workpiece and the secondary or false cathode has a value between zero and the tension of dissolving of the workpiece in the particular electrolyte employed.

To enable the invention to be more clearly understood, some embodiments in accordance therewith will now be described by way of example with reference to the accompanying drawings, in which:

FIGURE 1 is a diagrammatic representation of an electrolytic cell showing the principles of the invention; and

FIGURES 2 to 6 each shows diagrammatic vertical cross sections through different electrolytic cells operated by the principles of the invention.

Referring to FIGURE 1 of the drawings, the workpiece B, one face of which is to receive a deposit, is deposed in the electrolyte of an electrolytic cell. The workpiece B is made the cathode between an anode A and a secondary or false cathode C. The cell is thus separated into two zones, a first zone containing the electrolyte between A and B, and a second zone containing the electrolyte between B and C. It will be noted that by connecting the positive pole of the cell electric circuit to A and the negative pole to C, the workpiece B is joined in series through the electrolyte and becomes negative on the front which is to have the deposit applied thereon, e.g., to be metallized, and positive on the back or reverse which is to be kept free of any deposit thereon.

Let U be the difference of electric potential between C and B. It has been established on the one hand that if U is equal to or greater than the tension of dissolving the metal forming the positive face of B in the particular electrolyte employed, this face will be attacked or spotted, and on the other hand if U tends towards zero, the positive polarity of said face of B also tends towards zero, and consequently that said face, namely the negative face B, tends to become covered with the metal deposited on the front face. From this it has been deduced, that U should lie between these two limiting values if the deposition of metal on the positive face of B of the workpiece is to be avoided during the electrolysis.

To adjust U, one of the three following methods, diagrammatically shown in FIGURES 2, 3 and 4, may be employed.

Referring to FIGURE 2, the electrolysis cell container of steel plate forms the secondary cathode C. The distance C–B being stipulated, the greater proportion of the current between C and B is drawn off by means of a resistance bridge R'. Let R be the resistance of the electrolyte lying between C and B; R' is made smaller than R in such manner as to obtain a very strong current I in the shunt and a current I' in the electrolyte lying between B and C which is very weak, but nevertheless sufficient to trap wandering ions and to deposit these on the false cathode C.

Referring to FIGURE 3, the electrolysis cell container also forms the secondary cathode C. The distance C–B is specified. Two branches are established between the points D and B, of which one D–O–B has a resistance Rc (resistance of the conductor and of the contact), and another D–F–C–B, of which the resistance is equal to $R'+R'c+R$. Rc must be made smaller than $R'+R'c+R$ in such manner as to produce in the electrolyte lying between B and C a current I' which is very weak, but nevertheless sufficient to trap the wandering ions and to deposit them on the false cathode C.

Referring to FIGURE 4, the electrolysis cell container still forms the secondary cathode C. A shunt is not employed, but a movement I' is artificially and periodically produced which is very weak, in the electrolyte lying between B and C in order to trap the wandering ions and to deposit them on the false cathode. For this purpose, the positive phase is directly applied to the anode A, the negative phase being supplied alternatingly with a longer period to the cathode B (the pieces which are to be metallized being formed by a stack of bearings in this FIGURE 4) and with a short period (after having passed between D and C through a resistance R'), to the secondary cathode. During the long period, the exterior and interior faces of the bearings form a cathode, and the interior face tends to acquire an electrolytical deposit. During the short period, the cell container forms the cathode and the bearings are connected in series between C and A, the exterior face being a cathode and the interior face an anode.

R1 and R2 correspondingly mark the resistance of the electrolyte between C and B and between B and A, and if U is the tension applied across the terminals A and B during the long period, the following equation applies:

$$I=\frac{U}{R2}$$

and during the short period, if the same tension is applied across C and A:

$$I'=\frac{U}{R'+R1+R2}$$

R' is generally determined in such manner that $I=10I'$. The potential difference I'R1 between C and B is thus very small.

The ratio: long period/short period of which the mean value is equal to 10, is determined empirically and controlled by means of a timing mechanism shown diagrammatically in FIGURE 4.

Referring to FIGURE 5, this shows a disposition wherein electro-deposition may be performed on one face with a periodical reversal of current.

During the long period, the positive pole is connected to A; the negative pole is connected to O with shunts at ODB and ORC. During the short period, the positive pole is connected to O with shunts at ODB and ORC; the negative pole is connected to A.

The current I' has practically the same value during the long period and during the short period, and the electric potential difference between C and B which is periodically reversed, and should have a value (controlled by means of the variable resistance R) such that it lies between O on the one hand and the tension of dissolving of the metal forming the face which is to be protected, and on the other hand between O and the tension of deposition of the metal which is to be electroplated.

Referring to FIGURE 6, this shows the disposition in series of 3 cells constructed as shown in FIGURE 3.

As shown in FIGURES 1–6, the secondary cathode is shielded from direct flow of current from the anode. In the case of FIGURE 1, supporting partitions E and E' provide the shield with partition E' made from polyvinyl chloride extending deeper into the electrolyte than the anode A. Regarding the embodiments of FIGURES 2–6, the secondary cathode is the container for the cell and the anode is disposed centrally of the stack of bearings which shield the secondary cathode from direct current flow from the anode for that portion of the anode immersed in the electrolyte. Also, a bottom member upon which rests the bottom bearing of the stack is interposed between the secondary cathode and the anode.

As hereinabove set forth, the process makes it possible to employ the electrolytic cell container itself as a secondary or false cathode, said container thus being self-protected against acid baths wherein the metal deposited is but weakly attacked.

The cell container may then be made of materials of low cost. It is thus for example, possible to employ simple iron containers for the electrolytical deposition of lead from an electrolytic bath based on lead fluoborate.

The process of the invention ensures in a very simple manner effective protection of the surfaces of metal workpieces which it is not intended to receive a deposit. If the piece which is to be processed has a complex shape or if its exterior or interior and inner and outer parts are provided with communication passages, as for example bearings having greasing orifices, the internal surface of the workpiece should be leaded after having received a lining of fritted or sintered copper-lead.

The invention will now be further described by way of example with reference to the following examples:

Example 1

For producing a lining of lead-tin deposit inside bearing halves.

An electrolytic bath of the following composition was used:

	G./l.
Lead fluoborate	410
Tin fluoborate	43
Free fluoboric acid	80
Gelatine	3

14 bearings B, being 28 bearing halves assembled in pairs, with cleavage plane against cleavage plane, were disposed in this electrolyte as shown in FIGURE 2. Having an inner diameter of 100 mm., an outer diameter of 107 mm., and a width of 32 mm., the bearings were each formed by a backing of mild steel of 3 mm. thickness, which was internally coated with a lining of copper-lead having a thickness of 0.5 mm. Each of the bearings was pierced by two greasing holes having a diameter of 9 mm.

Operating as a cathode, the part which was to be leaded formed by the copper-lead lining facing towards the anode

A and the steel backing being the part not intended to be metallized, these bearings were immersed in a cylindrical container made of steel sheet of 2 mm. thickness, 180 mm. diameter and 550 mm. high, forming a secondary cathode.

The cell thus formed was supplied under an electric potential difference U of 1.25 volts with a current density of 2.15 amp./dm.^{2}. The potential difference U' between the positive faces of the bearings, that is to say the parts not intended to be metallized, and the secondary cathode, was fixed at 30 mv. In these conditions, the resistance R' of the shunt I–D amounted to 0.001 ohm and the intensity of the current I' to 30 amp.; the resistance of the electrolyte between C and B amounted to 0.03 ohm and the current I to 1 amp. The intensity used for the protection of the rear face of the bearing thus represented 3.54% of the total intensity.

After 60 minutes of operation, the bearings were removed from the electrolysis vat. The quantity of lead-tin deposited on the face to be leaded amounted to 82 milligrams per square centimeter. The part not intended to be metallized did not exhibit any trace of leading or of electrolytic attack.

Example 2

For internal leading of a bush.

An electrolytical bath of the following composition was utilized:

	G./l.
Lead fluoborate	400
Free fluoboric acid	80
Free boric acid	25
Gelatine	2

10 bushings B, having an inner diameter of 60 mm., an outer diameter of 67 mm. and a width of 40 mm., formed by a backing of mild steel of 3 mm. thickness internally coated with a bronze lining containing 80% of copper, 10% of lead, 10% of tin, were disposed according to FIGURE 3. Each was pierced by a greasing hole having a diameter of 8 mm.

The bushings acted as a cathode, the part to be leaded being formed by the bronze lining facing towards the anode A, the steel backing being the part not intended to be metallized.

These bushings were immersed in a cell having a cylindrical container of sheet steel of 2 mm. thickness, having a diameter of 125 mm. and a height of 450 mm. operating as a secondary cathode C.

The cell was supplied under an electric potential difference U of 1.25 volts, with a current density of 2 amps./dm.^{2}. The potential difference U' between the positive faces of the bushings, that is to say of the parts not intended to be metallized, and the secondary cathode C, was fixed at 10 mv. In these conditions, the total resistance of the shunt D–F–C was equal to the sum of:

R' (resistance of the shunt)	0.010
R'c (resistance of the contact and of the conductor)	0.003
R (resistance of the electrolyte)	0.007
	or 0.020 ohm

The resistance of the shunt D–B was equal to the resistance Rc (resistance of the contact and of the conductor), or 0.003 ohm. The intensity I' was equal to 0.5 amp. and the intensity I to 15 amp. The intensity used for the protection of the rear face of the bearing thus represented 3.2% of the total intensity.

After 60 minutes of operation, the quantity of lead deposited on the face to be leaded amounted to 76 milligrams per square centimeter. The part not to be metallized did not bear any trace of deposit or of electrolytic attack.

Example 3

For producing a deposited lining of lead-tin inside bearing halves.

A bath of the following composition was utilized:

	G./l.
Lead fluoborate	450
Tin fluoborate	50
Free fluoboric acid	90
Free boric acid	30
Gelatine	2

6 bearing halves B, disposed according to FIGURE 4, having an inner diameter of 158 mm. and outer diameter of 178 mm., a width of 140 mm. were formed by a backing of mild steel of a thickness of 7.5 mm. internally coated with a lining of copper-lead of a thickness of 2.5 mm. 3 bearing halves were each pierced by a hole of 12 mm. diameter, the 3 others by 2 holes of 12 mm. diameter.

The bearing halves acted as a cathode, the part to be leaded formed by the copper-lead lining facing towards the anode A, and the steel backing being the part not to be metallized. They were immersed in a cylindrical vat C made of steel having a thickness of 3 mm., a diameter of 250 mm. and a height of 500 mm. forming the secondary cathode.

The difference of electric potential applied across B and A and across C and A amounted to 1.10 volts. During the long period, the cathodic current density amounted to 3.5 amp./dm.^{2}. The resistance of the cell between A and B amounted to 0.015 ohm, the intensity I to 73 amp. In the short period circuit, R'=0.139 ohm, $R1$=0.003 ohm, $R2$=0.015 ohm. The intensity I' was equal to 7 amp., and the potential difference U' between C and B, that is to say between the positive faces of the bearings (not to be metallized) and the secondary cathode C amounted to 21 mv. The duration per minute of the long period amounted to 50 seconds as against 10 seconds for the short period. The intensity utilized for the protection of the rear face of the bearing thus represented 1.88% of the total intensity applied.

After 60 minutes of operation, the quantity of lead deposited amounted to 135 milligrams per square centimeter. The part not to be metallized was free of any trace of lead and corrosion.

Example 4

For coppering a mild steel sheet on one face only according to FIGURE 1.

An electrolytic bath of the following composition was used:

	G./l.
Copper cyanide	64
Free sodium cyanide	6.25
Sodium bisulphite	3.10

The sheet B to be coppered consisted of a strip having a length of 2500 mm., a width of 100 mm., and a thickness of 2.5 mm. being carried between the supporting partitions E which was movable and E' which was fixed, said partitions being made of polyvinyl chloride. These latter could at will hermetically divide the vat into two compartments if the vat F is utilized as the spurious cathode, or non-hermetically if a separate spurious cathode is utilized. The sheet formed the cathode and had the face to be coppered turned towards the anode A. The latter was made of 10 rectangular copper electrodes having a length of 250 mm., a width of 200 mm. and a thickness of 8 mm., immersed in the bath and suspended from a busbar. The secondary cathode C was formed by a strip of sheet steel having a width of 150 mm., a length of 2500 mm., and a thickness of 2 mm. The cell was supplied with direct current under 6 volts, with a current density of 2 amp./dm.^{2}. The potential difference between the positive face of the sheet B and the secondary cathode C amounted to 200 mv.

After 7 minutes of operation, the quantity of copper deposited amounted to 8 milligrams per square centimeter. The part not to be metallized did not bear any trace of deposit or of electrolytic attack.

I claim:

1. A process for producing an electrolytic deposit on only one face of two substantially parallel faces of a workpiece while avoiding formation of said deposit on said second face of said workpiece comprising disposing said workpiece as a cathode in an electrolyte of an electrolytic cell between the anode of said cell and a secondary cathode with said one face of said workpiece on which the deposit is to be effected directed toward said anode, said secondary cathode being the container of said cell, substantially shielding said secondary cathode from direct flow of current from said anode, providing one of a shunt which includes a resistance between said workpiece and said secondary cathode and of a resistance in series with said workpiece and said secondary cathode such that the electrical potential between said workpiece and said secondary cathode has a value between zero and the tension of dissolving of said workpiece in the electrolyte employed and such that the current between said workpiece and said secondary cathode is sufficient to trap wandering ions on said secondary cathode.

2. The process of claim **1** characterized by producing a weak current periodically between said workpiece and said secondary cathode through applying a negative polarity for a long period upon said workpiece and for a short period upon said secondary cathode.

3. A process for producing an electrolytic deposit on only one face of two substantially parallel faces of a workpiece while avoiding formation of said deposit on said second face of said workpiece, comprising disposing said workpiece as a cathode in an electrolyte of an electrolytic cell between the anode of said cell and the secondary cathode with said one face of said workpiece on which the deposit is to be effected directed toward said anode, said secondary cathode being the container of said cell, substantially shielding said secondary cathode from direct flow of current from said anode, providing one of a shunt which includes a resistance between said workpiece and said secondary cathode and of a resistance in series with said workpiece and said secondary cathode, during a long period of time applying between said workpiece and said secondary cathode an electrical potential which has a value between zero and the tension of dissolving said workpiece in the electrolyte; during a short period of time reversing said electrical potential between said secondary cathode and said workpiece and making same between zero and the tension of deposition of the metal which is to be deposited and applying a positive polarity to said secondary cathode and a negative polarity to said anode.

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