May 10, 1955 | A. W. HOLMES ET AL | 2,708,181

ELECTROPLATING PROCESS

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Fig. 1.

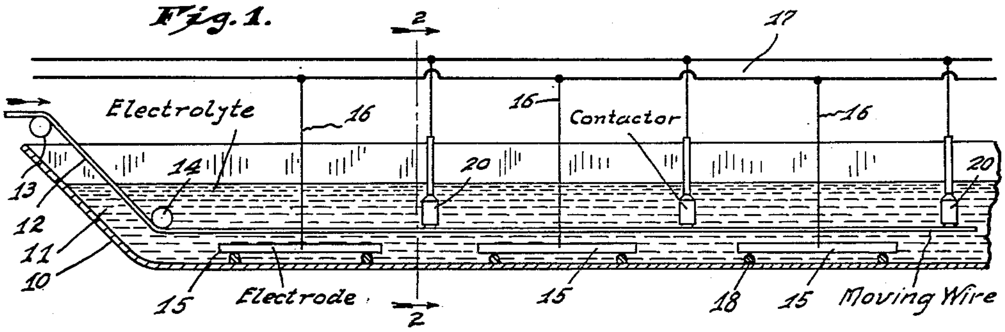


Fig. 2.

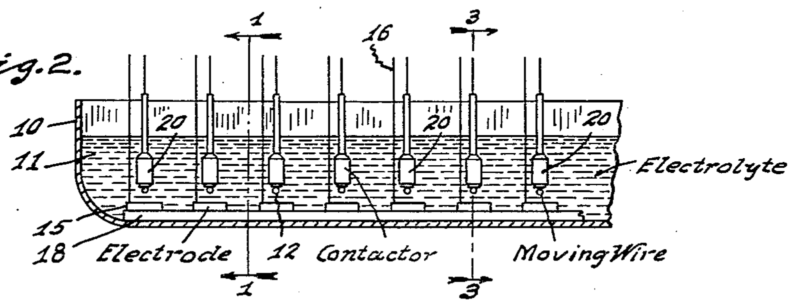
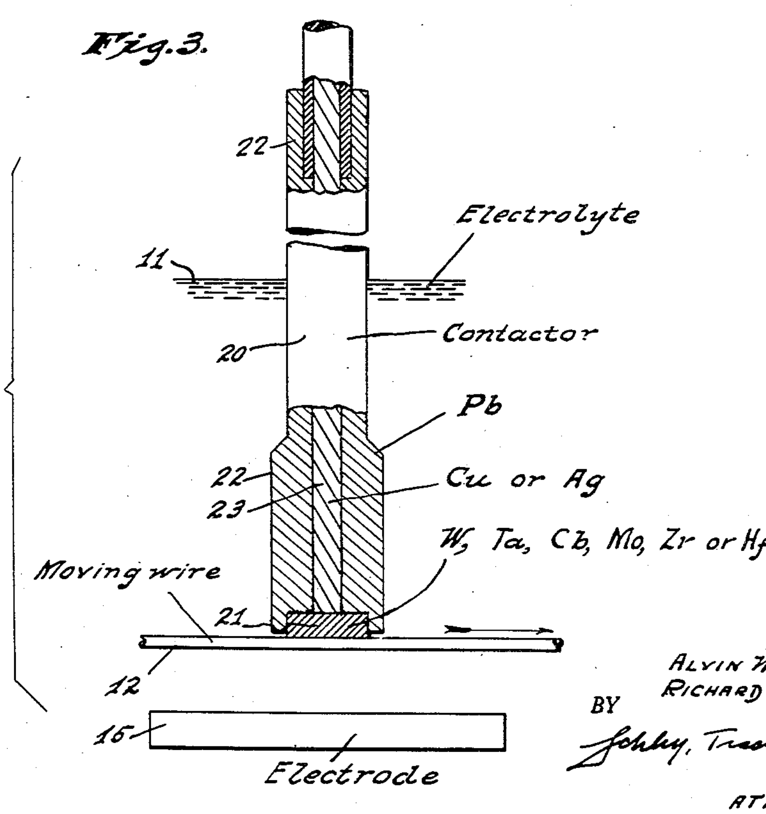


Fig. 3.



INVENTORS.
ALVIN W. HOLMES and
RICHARD K. BURNS,
BY
Johley, Trask, & Jenkins
ATTORNEYS.

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ELECTROPLATING PROCESS

Alvin W. Holmes and Richard H. Burns, Muncie, Ind., assignors to Indiana Steel & Wire Company, Inc., a corporation of Indiana

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9 Claims. (Cl. 204—28)

Our invention relates to an electrolytic process and apparatus, and especially to a contactor for under-liquid electric-current-supplying engagement with articles, especially metal articles, serving as moving electrodes (cathodes or anodes) in an electrolyte; as for instance in electroplating, or in electro-cleaning or electro-polishing or both.

Our contactor is particularly applicable for supplying current to the submerged portions of such things as moving metal wire, metal sheet, or metal strip fed continuously into and through and then out of an electrolyte in a tank. The electrolyte may be of any desired or suitable character, such as is used in electro-plating, or in electro-cleaning or electro-polishing, whether acid, neutral, or alkaline.

Our invention is of especial advantage in electroplating; more especially when the metal to be electrically deposited is zinc; although it is also very advantageous when the electrodeposition is of other metals, such for instance as cobalt, nickel, cadmium, copper, chromium, and tin. It is of very great advantage in electroplating from an ammoniacal solution, as for instance in the electrodeposition of zinc from a solution of a zinc-tetramine salt, for example zinc-tetramine chloride, such as is used in the Hubbell and Weisberg Patent No. 2,200,987, granted May 14, 1940.

We have discovered that in electroplating, especially of zinc from such an ammoniacal solution, the metal being electrodeposited tends to build up objectionably on ordinary contactors by which current is supplied to the submerged moving article to be plated, particularly at and near the area of contact of the contactors with that moving article; and that this built-up metal often becomes so hard and of such rough pinnacle-like character that it both separates the contactor-body from the moving article being plated and produces scratches in the surface being plated of that moving article. The amount of this building up of the objectionably hard scratching projections depends upon the metal used for the contactors, but such building up occurs when the contactors are made of any of the more common metals.

Thus in the electroplating of zinc, especially from a solution of zinc-tetramine salt, ridges or pinnacles of very hard zinc tend to form on the surface of the contactor at and near the vicinity of the contact area, and scratch and mar the surface being plated, such as the surface of wire or sheet or strip. These pinnacles are not only hard and pointed, but are very difficult to remove; and generally are not removable by the pressure between the contactor and the moving article as the latter is moved through the electrolyte in contact with the contactor.

We have discovered that if we make the contactors in electroplating, or those surfaces thereof which engage the moving article serving as the electrode (the cathode in electroplating), predominantly of metal having atomic weight between 85 and 190 and in the heavy-metal sub-groups of groups IV, V, and VI of the periodic system, we largely and sometimes substantially wholly eliminate the tendency to form these scratching projections of deposited metal; and that instead we both lessen the amount of metal deposited on the contactors and change the character of whatever small amount of metal is so deposited from hard and scratching tenacious pinnacles to a comparatively soft and easily removable mass, which wipes off so easily by contact with the moving articles being plated that little and often no building up of deposited metal on the contactors develops.

The metals having atomic weights between 85 and 190 and in the heavy-metal sub-groups of groups IV, V, and VI of the periodic system are the six metals: tungsten, tantalum, columbium, molybdenum, zirconium, and hafnium. Our preference among these six metals is in the order in which they are just named.

We have also discovered that the first four of these same metals—tungsten, tantalum, columbium, and molybdenum—are especially suitable for the contact metal when the contactors engage submerged moving articles in electro-cleaning and electro polishing operations, as in anodic cleaning and polishing of wire, strip, and sheet. Such electro-cleaning and electro-polishing are most commonly done with an acid electrolyte, and with moving articles connected as anodes; and these four metals are particularly desirable because the acid of the electrolyte has very little effect upon them, and they last for long periods without need for replacement.

Thus the four metals tungsten, tantalum, columbium, and molybdenum of groups V and VI are of great advantage both when the moving electrode in the electrolyte is a cathode and when it is an anode; and the two metals zirconium and hafnium of group IV are of great advantage when that moving electrode is a cathode.

This is most surprising, and especially so when the moving electrode is a cathode; since it is impossible to foretell the reduction in amount and the change in character of the deposited metal, and the avoidance of sharp hard pinnacles, on the cathode contactors, or the permanency of these metals in an electrolyte.

Since these six metals are all rather expensive, it is generally convenient to use them only for the actual contacting portion of the contactor, and to connect that contacting portion to the electric circuit by some suitable conducting metal, such as copper or silver, encased in a protecting sheath which also supports the contacting portion with its contacting surface exposed. The protecting sheath may be of some relatively inert metal, most conveniently lead, or of some insulating material, such as a plastic which will resist attack by the electrolyte. We prefer to have a sliding contact between the contactor and the moving electrode, and so illustrate our invention for the electroplating of wire; but our invention is not limited to sliding-contact contactors.

The accompanying drawing illustrates our invention, as applied in the electrolytic treatment of wire. In such drawing, Fig. 1 is a partial longitudinal schematic section, substantially on the line 1—1 of Fig. 2, through an electrolytic bath in which the wire is treated, showing several of our contactors in under-liquid electric-current-supplying engagement with one of the moving wires; Fig. 2 is a partial transverse schematic section through the electrolytic unit of Fig. 1, taken substantially on the line 2—2 of Fig. 1; and Fig. 3 is an enlarged elevation of a preferred form of one of our contactors, in place in the electrolytic bath, in partial section on the line 3—3 of Fig. 2.

The electrolytic bath can be of any desired construction. It has the usual tank **10** of any convenient material, containing an electrolyte **11**, through which any number of wires **12** to be electrolytically treated are continuously moved lengthwise in well-known manner. The wires 12 conveniently enter and leave the electrolyte 11 in the tank 10 over rollers 13 and 14, of well-known construction.

Suitably supported within the tank 10, in contact with the electrolyte 11, are any desired number of stationary electrodes 15, of any desired character. For instance, in electroplating they may be of the metal to be plated, in which case they are anodes to supply the metal for the electrolyte; or they may be of some other material, as when the metal for the electroplating electrolyte is supplied otherwise than from such stationary electrodes 15 as is done in the process of the aforesaid Hubbell and Weisberg Patent No. 2,200,987, for instance when they are of magnetite as are the anodes in electroplating Patents Nos. 2,393,516 and 2,393,517, granted January 22, 1946, in the name of one of us (Burns), or when they are cathodes in electro-cleaning or electro-polishing. The stationary electrodes 15 are shown resting on ridges or cross-bars 18 provided on the bottom of the tank 10; but that is only schematic, and any other method of supporting the stationary electrodes may be used. The stationary electrodes 15 are suitably connected, in parallel, as by wires 16, to one side of an electric circuit 17 of suitable voltage—to the positive side of a direct-current circuit in electroplating, and most commonly to the negative side of a direct-current circuit in electro-cleaning and electro-polishing.

The moving wires 12 form the other electrode—the cathode in electroplating, and usually the anode in electro-cleaning and electro-polishing. As is well understood, the passage of current through the electrolyte between the stationary electrodes 15 and the moving wires 12 produces the desired treatment, such as deposition or removal of metal. The moving wires 12 are connected to one side of the aforesaid electric circuit 17—the other side from that to which the stationary electrodes 15 are connected—by the contactors 20 which embody our invention.

One of these contactors is shown in Fig. 3. Its essential part embodying our invention in its preferred form is an engaging portion 21 against the exposed surface of which one of the moving wires 12 rubs as it travels lengthwise through the tank 10. There may be any desired number of these contactors 20, but there is always one and usually a plurality of them in contact with each wire 12. The engaging portion 21 of each contactor is shown mounted in an inert-metal sheath 22, as of lead, in the end of which it is so embedded that it has one surface exposed for rubbing engagement with the moving wire 12; and is shown connected to the electric circuit by a conducting bar 23, as of copper or silver, extending lengthwise through a sheath 22 and out through the upper end thereof to provide the connection to the proper side of said electric circuit—the negative side in electroplating. The conducting bar 23 is suitably attached, as by welding, brazing, or soldering, to the contacting portion 21, to hold the latter in place in the end of the sheath 22 and to provide good electrical connections.

The contacting portion 21, or at least its wire-engaging portion, is made predominantly, or wholly, of metal having atomic weight between 85 and 190 and in the heavy-metal sub-groups of groups IV, V, and VI of the periodic system. Such metals are tungsten, tantalum, columbium, molybdenum, zirconium, and hafnium, listed in the order of their preference. These six metals are all effective for our purposes in electroplating; and the first four of them are effective both in electroplating and in electro-cleaning and electro-polishing. In electroplating all six avoid or substantially avoid the depositing on the contactor of hard adherent ridges and pinnacles of the coating metal, and cause whatever small deposits are so made to be a soft and easily removable mass—a most surprising and unforeseeable effect. As cathodes all six are substantially inert chemically in the various electrolytes which may be used, so that they dissolve very little in the electrolyte, and do not contaminate it; and the first four of them are substantially inert chemically in such electrolytes even when the current is off or when they are anodes, and so do not contaminate the electrolyte either in electroplating or in electro-cleaning or electro-polishing. In addition, the first four—those of groups V and VI—metals are fairly hard, so that the moving wires wear into them very little, and they will last for months if not indefinitely.

The electrolyte 11 may be alkaline or neutral or acid; although in electroplating the acidity should not be so great that it causes rapid re-solution of the deposited metal. In electroplating the electrolyte is a solution of a salt of the metal to be deposited; and it can conveniently be a solution of a complex metal salt, such as zinc-tetramine chloride when zinc is the metal to be deposited, or complex salts of ammonia with cobalt or with nickel or with cadmium if those are the metals to be deposited.

In operation, the moving wires 12 or other moving articles to be electro-treated are caused to travel through the electrolyte 11, lengthwise in the case of wire or sheet or strip, in contact with the work-engaging portions 21 of the contactors 20. The current from the electric circuit 17 causes ion migration through the electrolyte between the stationary electrodes 15 and the moving articles 12, as to deposit metal on the latter in electroplating and to remove metal therefrom in electro-cleaning and electro-polishing. The depositing of such metal in electroplating makes a smooth coating on the moving article to be coated, and the metal is deposited quite efficiently; because there is little or no depositing of metal on the contactors, and no building up of pinnacles or ridges on the work-engaging surfaces of the contactors to cause scratching or other marring of the surface of the article being plated.

We claim as our invention:

1. The process of electroplating a metal article with metal, consisting in mechanically moving that metal article through an electrolyte containing in solution a salt of the metal to be deposited, passing an electric current through said electrolyte with said metal article as the cathode, and supplying said electric current to said metal article by a contactor with which said moving article is in rubbing engagement within the electrolyte, the article-engaging portion of said contactor being made of at least one metal from the group consisting of tungsten, molybdenum, tantalum, columbium, zirconium, and hafnium.

2. The process of electroplating a metal article with metal as set forth in claim 1, in which the article-engaging portion of the contactor is made of at least one metal from the group consisting of tungsten and molybdenum.

3. The process of electroplating a metal article with metal as set forth in claim 1, in which the article-engaging portion of the contactor is made predominantly of tungsten.

4. The process of electroplating a metal article with metal as set forth in claim 1, in which the article-engaging portion of the contactor is made predominantly of molybdenum.

5. The process of electroplating a metal article with metal as set forth in claim 1, in which the article-engaging portion of the contactor is made predominantly of tantalum.

6. The process of electroplating a metal article with metal as set forth in claim 1, in which the electrolyte is an ammoniacal electrolyte.

7. The process of electroplating a metal article with metal as set forth in claim 1, in which the electrolyte is an ammoniacal electrolyte, and the article-engaging portion of the contactor is made predominantly of tungsten.

8. The process of electroplating a metal article with zinc, consisting in mechanically moving that metal article through an ammoniacal electrolyte containing in solution a zinc-tetramine salt, passing an electric current through

said electrolyte with said metal article as the cathode, and supplying said electric current to said metal article by a contactor with which said moving article is in rubbing engagement within the electrolyte, the article-engaging portion of said contactor being made of at least one metal from the group consisting of tungsten, molybdenum, tantalum, columbium, zirconium, and hafnium.

9. The process of electroplating a metal article with zinc as set forth in claim 8, in which the article-engaging portion of the contactor is made predominantly of tungsten.

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