METHOD FOR REMOVAL OF ADHERENT SURFACE COATINGS FROM SUBSTRATES

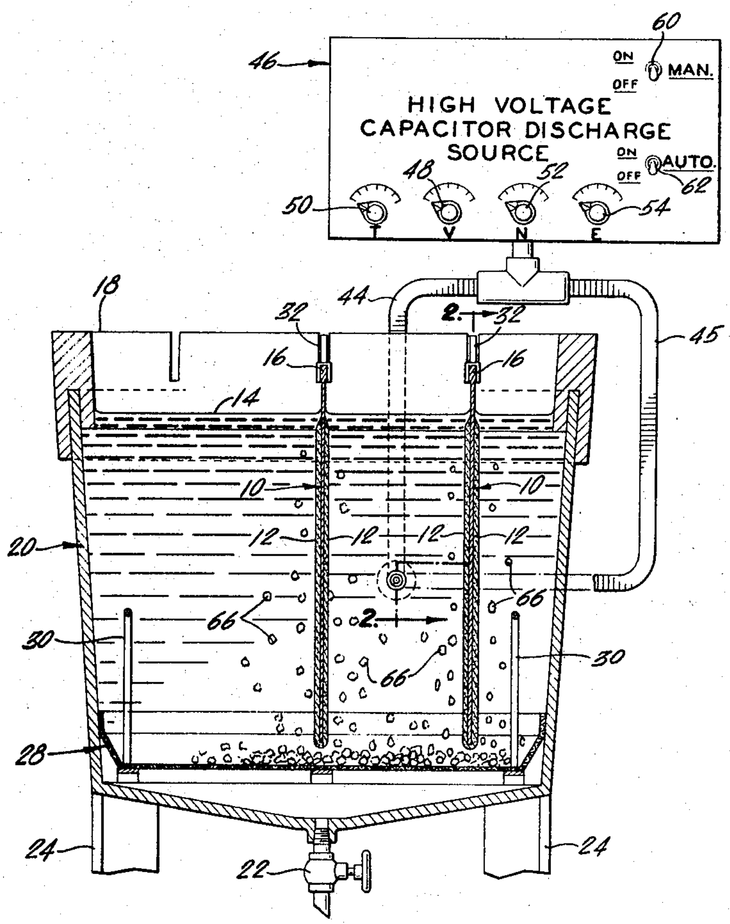

FIG. 1.

FIG. 2.

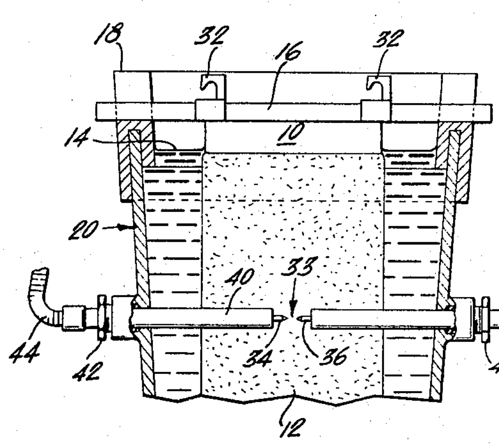

FIG. 3.

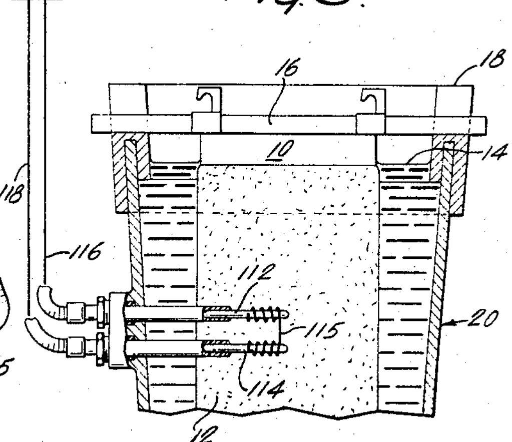

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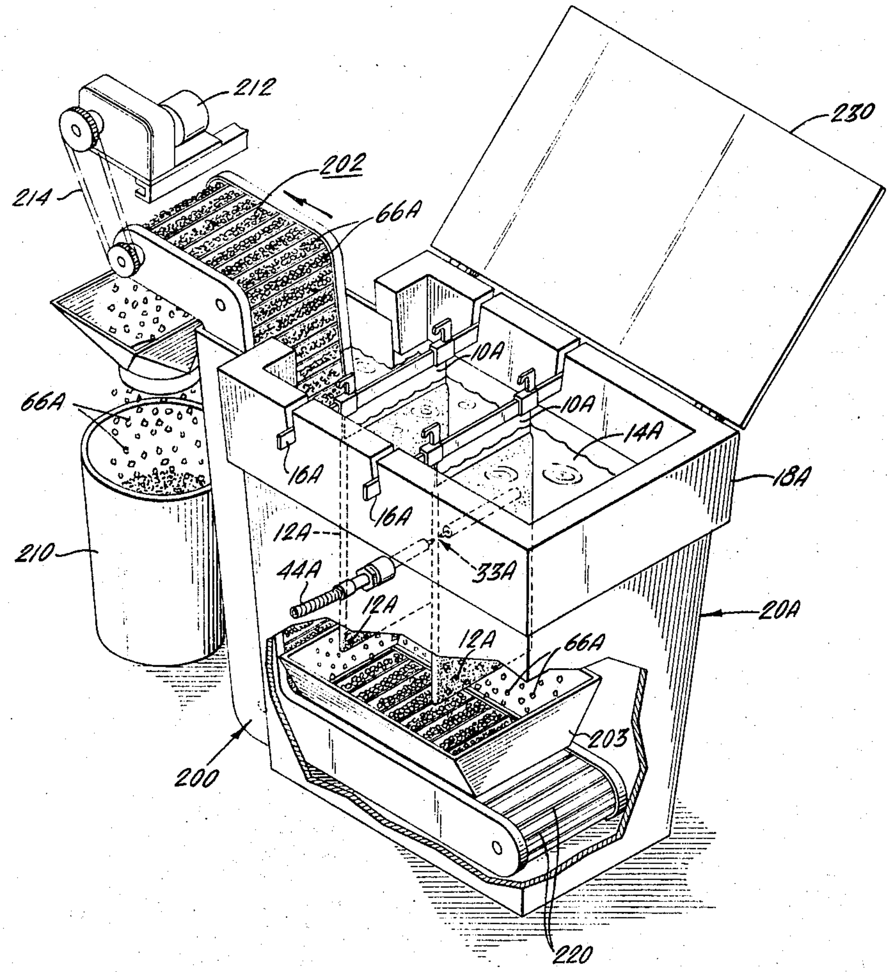
FIG. 4



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METHOD FOR REMOVAL OF ADHERENT SURFACE COATINGS FROM SUBSTRATES

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ABSTRACT OF THE DISCLOSURE

A method of removing electrolytically-deposited manganese from re-usable cathode plates by immersing the cathode plates in a liquid and producing one or more electro-hydraulic shock waves in the liquid which pass through the liquid and impinge the coated plates, causing the manganese to fall away from the plates for collection and removal. Preferably, the shock wave is generated by discharge of a capacitor across a spark gap in the liquid.

This invention relates to methods for removing adherent surface coatings from substrates, and especially to methods for removing electrolytically-deposited material, such as manganese, from cathodes.

It is known to produce certain materials, such as manganese, by electrolytically depositing them upon cathode elements such as metal plates and then stripping material from the plates, after which the plates are used again as cathodes in subsequent electrolytic deposition of the material.

A variety of methods have been proposed and utilized for removing such deposited materials from the cathode plates, as by striking the plates or flexing them manually or automatically. Such methods have a tendency to deform the plates permanently. U.S. Patent No. 3,094,437 describes a method in which mechanical vibrations are applied to one end of the deposit-coated cathode to cause it to flex, thus separating the deposited metal from the cathode; with the latter method of stripping the cathode, the permanent deformation of the cathode which occurred with some of the previous processes is minimized. Regardless of how it is produced, any such permanent deformation of the plates introduces the difficulty that, when the deformed cathode is re-used, non-uniform electrolyzing currents are produced during deposition with consequent losses in the efficiency and quality of the deposit. While as mentioned above this undesirable effect is minimized by the process described in Patent No. 3,094,437, the method and apparatus employed in the latter process is relatively complex and requires substantial maintenance. In addition, since the removal of the material by these previous methods requires substantial flexing of the cathode, the cathode must be relatively thin and flexible and hence is undesirably susceptible to such permanent deformation, either during the removal of the material or accidentally during handling. Prior methods have generally also required application of a separating layer, such as buffed wax, to the cathode plate prior to plating thereof, which process is time-consuming and critical.

Accordingly it is an object of the invention to provide a new and useful method for removing adherent surface coatings from substrates.

Another object is to provide a new and useful method

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for removing material electrolytically-deposited upon a cathode substrate.

Another object is to provide such a method which can be practiced without producing permanent deformation of the substrate.

A further object is to provide such a method which can be performed rapidly and lends itself to automatic control.

It is another object to provide such a method which is effective in removing electro-deposited materials even from rigid cathodes.

It is still another object to provide such a method which is effective in removing electrolytically-deposited manganese from metal cathodes even where the manganese is deposited directly on the cathode without an intervening layer having been provided between the deposit and the cathode.

Still another object is to provide such a method which can be performed economically.

In accordance with the invention the above objects are achieved by immersing a substrate having a surface coating thereon in a liquid, and then generating at least one hydraulic shock wave in the liquid, at a position spaced from said coating and substrate, in sufficient intensity to impinge on said coating and separate it from said substrate. Preferably, each of the one or more hydraulic shock waves is generated by passing a short pulse of high-intensity electrical current across a spark gap in the liquid, or through a relatively fine wire which explodes or vaporizes in response to the pulse. The equipment used to generate the hydraulic shock waves may be of the general kind which has previously been employed for the high-velocity forming of metals, in which the electrical pulse is produced by the discharge of capacitive means across the spark gap or through the wire. The effect of this shock-wave treatment is to strip the surface coating from the substrate without damaging or permanently deforming the substrate, the stripped coating typically falling from the substrate to a collecting system for removal from the liquid.

In one preferred form of the invention, the coating to be removed comprises manganese electrolytically-deposited upon a metal cathode, which cathode may be of stainless steel or hard aluminum, for example, and may be so thick as to be rigid. Although a wax buffing of the cathode before electrolytic deposition thereon may be performed, it is one feature of the invention that this step is unnecessary since the material can be automatically removed from the cathode by the method of the invention even through it is deposited directly upon the cathode metal.

These and other objects and features of the invention will be more fully comprehended from a consideration of the following detailed description, taken in connection with the accompanying drawings, in which:

FIGURE 1 is an elevational view, partly in section, of one form of apparatus suitable for performing the method of the invention;

FIGURE 2 is a fragmentary sectional view taken along the line 2—2 of FIGURE 1;

FIGURE 3 is a fragmentary sectional view similar to FIGURE 2, but showing an alternative form of apparatus for practicing the invention; and

FIGURE 4 is a perspective view showing another form of apparatus which may be used in practicing the invention.

Referring now to the particular embodiment of the invention which may be practiced by means of the apparatus shown in FIGURES 1 and 2, a pair of substrates are shown in the form of cathode plates **10** each having a coating **12** such as electrolytically-deposited manganese on both major surfaces thereof. The cathode plates **10** are submerged in a liquid **14**, which may be water, by means of a pair of suspending metal bars **16** secured to the plates and positioned in slots in a holder **18** mounted around the top of a tank **20** which contains the liquid **14**. The tank **20** may have a manually-controllable drain valve **22** at its bottom, and may be provided with a suitable stand **24** for accommodating the drain valve **22** above the surface on which the tank rests. A liquid-pervious hopper **28** is provided at the bottom of the tank **20** for catching and retaining the coating material separated from the cathode plates during the process. Appropriate handles **30** may be provided to permit ready removal of the hopper, and suitable hooks such as **32** may be provided on the plate supporting bars **16** to permit convenient handling of the cathode plates.

To separate the coating material **12** from the plates **10** a spark discharge is produced across the spark gap **33** between a first insulated metallic conductor **34** and a second insulated metallic conductor **36**, mounted from opposite sides of tank **20** and extending toward each other. The spark gap is positioned laterally equidistant from each of the cathode plates **10** and between them, and is also centered vertically and horizontally with respect to the plates. Conductor **34** is held and surrounded by an insulating jacket **40** which extends through one sidewall of tank **20** by way of a fluid-tight seal provided by a packing gland arrangement **42**. A similar fluid-tight mounting arrangement **43** is provided for conductor **36**.

High-voltage pulses for producing the spark discharge and the consequent electrohydraulic shock wave are applied between conductors **34** and **36** by way of a pair of flexible high-voltage cables **44** and **45**, respectively from a high-voltage capacitor discharge source **46**. Source **46** is designed to provide high-energy, short-duration electrical pulses. In the particular embodiment shown it includes a manually-adjustable voltage control **48** for permitting adjustment of the voltage of the pulses; a manually-variable timing control **50** for permitting manual selection of the time interval between successive pulses during automatic operation; a manually-variable pulse number control **52** for permitting manual selection of the number of pulses generated in each series during automatic operation; and a pulse energy control **54** for determining the energy of the discharge pulses. Also included in this embodiment are a two-position "Manual" switch **60** and a two-position "Automatic" switch **62**. The arrangement of source **46** is such that a single output pulse can be produced by an operator at will by each operation of the "Manual" switch **60** when the "Automatic" switch is in its OFF position; in this way, for example, an operator can observe the degree of separation of the plating **12** from the cathodes **10** and can operate manual switch **60** repetitively until a sufficiently complete degree of separation is observed. The nature of the pulses produced during such manual operation will be determined by the settings of the various controls **48**, **50** and **54**. Alternatively, a predetermined number of pulses may be generated and applied automatically to the spark gap by setting the control **52** for the desired number of pulses, and by then operating switch **62** to its ON position and leaving it there until the pulse series is ended.

It will be understood that the source **46** may take any of a large variety of forms in different applications of the invention. In particular, the nature of the controls used and the degree of automation embodied therein may vary widely from that specifically illustrated. Suitable types of such sources are available commercially and have been used in the high-velocity forming of metals by electrohydraulic shock waves, and one skilled in the art will be able to provide a suitable form of such apparatus for any given application. However, the form of source **46** which I prefer uses a suitable bank of high-voltage capacitors which are connected to a high-voltage DC charging source during intervals in which they are charged to a predetermined voltage, and are connected by appropriate electronic switch means, such as ignitrons to the spark gap **33** during each electrical pulse which produces an electrohydraulic shock wave. The pulse-energy control **54** selects the number of capacitors which are thus connected across the spark gap.

Each of the high-voltage pulses applied to the spark gap **33** produces a spark discharge, and each such spark discharge produces a transient electrohydraulic shock wave in the adjacent liquid **14**, which waves are of very high intensity and short duration and propagate through the liquid to impinge upon both of the cathode plates **10** and their coatings **12** in an intensity sufficient to cause the coating to separate from the plates, generally in the form of chips such as **66** which then fall into the hopper **28** and are collected. Furthermore, the coating on the cathode plates is thereby removed not only on the surfaces nearest the spark gap, but also from the opposite surfaces of the cathode plates. In some cases substantially complete removal of the coatings from all surfaces of the cathode plates can be achieved with only one or a few successive electrohydraulic shock waves, although in other cases ten or more shock waves may be required for best results. The durations of the electrical pulses are typically of the order of a few microseconds or less, although somewhat longer pulses can be used in some applications. The spacing of the spark gap from the plates **10** is sufficient that the shock wave spreads out relatively smoothly along the surface of the plates and removes the coating **12** without permanently deforming the plates.

While all of the details of the exact interaction which occurs between the shock wave and the coatings and cathode plates are not fully understood, it is believed that the extremely high-energy, short-duration shock waves impinging on the coatings on the cathode plates produce expansion-contraction waves in and into the coatings and plates which results in differential motion between the coatings and their respective supporting plates at the interfaces between them, whereby the coatings are loosened; however, the smooth distribution of the shock wave across the surfaces of the coatings and plates militates against any substantial local permanent deformation of the plates during the removal process.

Without thereby in any way limiting the scope of the invention, the following more detailed example is given of one preferred method for producing manganese which embodies the invention.

A plurality of type-316 stainless steel cathode plates 0.050 inch in thickness and 18″ by 36″ in area are plated in succession with manganese over their major surfaces in a standard arrangement for the electrolytic deposition of manganese. By way of example only, this may be accomplished by immersing a plurality of 1% silver-lead anode rods in an ammonium manganese sulphate bath, and immersing each stainless steel cathode plate in the bath while maintaining the anodes positive with respect to each cathode plate to produce the desired high-quality plated deposit of manganese on the cathode plate surfaces; typically, a current density of 45 amperes per square foot may be applied for 24 hours. As is common in such processes, a conventional porous diaphragm serving as a liquid barrier may be disposed around the cathode plate during this plating process. Typically, the resulting manganese deposit is $\frac{1}{16}$ of an inch or greater in thickness.

Prior to immersing the cathode plate in the plating bath, it may be cleaned by dipping it in acid, coated with a suitable wax, and then subjected to a buffing operation. However, it is one advantage of the present invention that the step of waxing and buffing may be omitted and the manganese plated directly upon the stainless steel, without preventing the subsequent removal of the manganese by the electrohydraulic shock wave treatment of the invention. Omission of the waxing and buffing step is not only a clear practical advantage in terms of savings of time and material, but also tends to overcome the lack of uniformity and reproducibility in plating and in removal of plating which commonly arises unless the waxing and buffing procedure is controlled with extreme accuracy.

The manganese-coated cathode plate is then lifted from the plating bath and is preferably dipped in a dichromate solution such as 10% sodium dichromate to prevent further oxidation and water staining. The cathode plate is then ready for application of the electrohydraulic stripping process.

In one preferred form of the process, as illustrated in FIGURES 1 and 2, two such manganese-plated cathode plates are suspended vertically in a water bath above an appropriate hopper for collecting the removed manganese. For example, the cathode plates may be placed about $9\frac{1}{4}$ inches apart and the pair of spark-discharge electrodes formed by the ends of the conductors **34** and **36** disposed about $4\frac{1}{8}$ inches from each cathode plate and centered vertically and horizontally with respect to both plates. The high-voltage capacitor discharge source **46** may then be adjusted to charge the capacitors therein to a voltage of about 12,000 volts, the controls thereof set to produce 15 pulses at the rate of three pulses per second, each pulse delivering approximately 2,000 joules, and the "Automatic" switch **62** turned to its ON position. The resultant 15 spark discharges produce 15 corresponding high-intensity transient electrohydraulic shock waves in sequence in the water, which waves impinge upon the coated cathode plates and cause the manganese thereon to fall in the form of chips from the plates into the hopper beneath. The percentage of removal of the manganese is typically near 100%, or within a few percent thereof, the percentage of manganese removal being in general even higher for the unwaxed, unbuffed cathode plates than for those which are waxed and buffed.

After a number of plates have been so stripped, the plates and the hopper containing the separated manganese may be removed from the water and dried to protect the final desired product. The plates may then be used again, i.e. re-plated and re-stripped a large number of times.

FIGURE 3 illustrates another arrangement which may be utilized for generating the electrohydraulic shock waves. In this arrangement a pair of high-voltage insulated rods **112** and **114** extend from the same wall of the tank **20** to a central position with respect to the cathode plates, and a relatively fine wire **115**, such as an aluminum wire of 50 mils diameter, is wound around and extends between the ends of the rods. The schematically-indicated connections **116** and **118** to rods **112** and **114** are supplied with the high-voltage pulses from the source **46** of FIGURE 1, the remainder of the apparatus being as shown in FIGURES 1 and 2. The process is then conducted in the manner described hereinbefore except that only manual, and not automatic, pulsing is used. The high-energy pulse discharge takes place initially along the path of the interconnecting wire **115**, which wire is thereby heated intensely so that it vaporizes almost immediately and is replaced by the spark discharge, the wire however serving accurately to define the path of the spark discharge. The latter arrangement is most conveniently applicable to systems which utilize a single spark discharge, or a series of spark discharges widely spaced in time, to permit replacement of the wire prior to each discharge.

FIGURE 4 shows apparatus for practicing the invention in a form which provides for continuous removal from the tank of the stripped material. It has been found that if the stripped material is allowed to remain in the tank for substantial periods of time while electrohydraulic shock waves continue to be generated, the additional shock waves tend to break up the previously-removed chips into finer pieces. However for certain purposes it is desired that the chips have a predetermined minimum size, e.g. $\frac{1}{2}$ square inch, and the desired size can be retained by automatically and continuously removing the chips shortly after they are stripped from the plates.

For this purpose the arrangement of FIGURE 4 includes a conveyor **200** including a continuous conveyor belt **202** which passes beneath the guide chute **203** upward and out of the liquid **14A** to drop the chips such as **66A** into any convenient receptable **210** for collection. Guide chute **203** serves to deflect and guide the chips onto the belt. The conveyor **200** may be of known type employing a suitable motor **212** and drive system **214** for continuously moving the conveyor belt **202** in the direction of the arrow. The belt **202** may be provided with suitable transverse ridges or bars such as **220** to aid in holding the chips during their ascent through the liquid.

The system of FIGURE 4 is otherwise generally similar to that of FIGURE 2, except that a hinged top door **230** which can be closed over the tank is also provided to prevent ejection of liquid of the bath from the tank **20A** by the shock waves. Parts of the arrangement of FIGURE 4 corresponding to those of the system of FIGURE 1 are indicated by the same numerals with the suffix A added thereto.

As indicated above, the precise form of the process utilized to apply the plating to the cathode plates is not critical to realizing advantages of the invention at least to some degree. The process may be applied to other plated metals, such as zinc, copper, chromium, cobalt or nickel, by way of example only. The material of the cathode plate also is not critical; for example, aluminum may be used in place of stainless steel, and in some applications plates of $\frac{1}{8}$ inch-thick, high-tempered aluminum alloy may be used to provide rigid cathode plates for use in the process. Other liquids than water may be utilized in the stripping process so long as they do not chemically affect the plated material or the cathodes adversely and so long as they provide the desired propagation of the electrohydraulic shock waves.

The number, form, spacing and energy level of the electrical pulses used in any given application is best determined by experiment while observing the effects thereof on the completeness of removal of the plated material.

It will therefore be appreciated that a process has been provided which is flexible and readily adaptable to a variety of applications, which can be performed rapidly, reproducibly and economically, which permits the omission of waxing and buffing steps which have been previously a source of expense and non-uniformity in prior stripping processes, which can be used with rigid cathode plates, and which is highly effective with respect to completeness of removal of plating without danger of permanent deformation of the cathode plates such as would interfere with their efficient re-use.

While the invention has been described with particular reference to specific embodiments thereof in the interest of complete definiteness, it will be understood that it may be embodied in a variety of diverse forms without departing from the spirit and scope of the invention as defined by the appended claims.

I claim:

1. The method of producing manganese which comprises the steps of electrolytically depositing manganese on a plurality of cathodes, immersing said cathodes and the manganese deposited thereon in a liquid, subjecting said cathodes to at least one electrohydraulic shock wave passing through said liquid to separate said manganese from said cathodes, collecting said separated manganese, and subsequently electrolytically depositing additional manganese on said cathodes.

2. The method of claim **1**, in which said liquid is water, said cathodes are rigid, and said cathodes are subjected to a plurality of electrohydraulic shock waves generated by a series of spark discharges between spark electrodes in said liquid.

3. The method of claim **1**, comprising the further step of continuously and automatically removing the separated manganese from below said cathodes to the exterior of said liquid.

4. The method of claim **1**, in which said manganese is deposited directly on a metal cathode without applying any intervening layer on said cathode.

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204—157.1; 134—1