A method of electropolishing utilizing a solution comprising a major amount of phosphoric acid, a minor amount of oxidizing component selected from chromium sesquioxide and a trivalent titanium oxide, and a minor amount of current supporting electrolyte. In particular embodiments, the electrolyte comprises ions of nickel and ions of one or more of iron and copper. The used bath can be reconstituted by the addition of phosphoric acid to adjust its specific gravity and may be purged of contamination by the addition of nickelous carbonate or by cathodic reduction. Use of the bath provides a monomolecular layer of metal oxide on the processed article.

13 Claims, 4 Drawing Figures
METHOD OF ELECTROPOLISHING

FIELD OF THE INVENTION

The fields of art to which the invention pertains includes the fields of electropolishing and chemical milling.

BACKGROUND AND SUMMARY OF THE INVENTION

A large variety of bath solutions are available for electropolishing and/or chemical milling of most industrial metals. Such baths as are presently known are generally limited in their application to the treatment of specific metals or limited groups of metals. There are no effective broad spectrum electropolishing and chemical milling baths which can be used for most industrial metals. Furthermore, prior baths generally require periodic replacement as they become contaminated from the articles being treated. Such contamination can take the form of excess metal ions from the surface of the article, NO$_2^-$, SO$_4^{2-}$, ions, halogen ions, or the like. As the bath solution evaporates or the active component is removed by "drag-out," replenishment results in a concentration of the contaminating ions so that upon each replenishment the useful life of the bath is substantially further reduced. In addition to the foregoing limitations, many prior art baths are formed with solutions of high vapor pressure resulting in in-plant contamination with toxic materials and with contamination of the outside environment when disposing of the bath solutions.

In particular, an electropolishing and chemical milling solution is provided comprising a major amount of phosphoric acid and a minor amount of oxidizing component selected from chromium sesquioxide and a trivalent titanium oxide. The bath solution contains supporting electrolytes such as Ni$^{2+}$, Fe$^{3+}$ and Cu$^{2+}$ ions which may be added initially to the bath solution or may be obtained in-situ during its operation. The solutions have broad spectrum utility for a wide variety of industrial metals, have an indefinitely long process life and minimal toxicity both in-plant and to the outside environment. Additionally, metal articles can be electropolished with substantially less processing time than with prior art baths and are often found to have unique surface characteristics as a result of such processing. Such characteristics include a brighter appearance, passivation against corrosion and much greater resistance to smudging than heretofore obtained.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic, plan view of an electropolishing bath for utilization of the novel solutions as provided herein;
FIG. 2 is a cross-sectional view of the bath taken on line 2--2 of FIG. 1, in the direction of the arrows;
FIG. 3 is a cross-sectional view of the bath taken on line 3--3 of FIG. 1, in the direction of the arrows; and
FIG. 4 is a schematic, cut-away of the surface region of an article electropolished utilizing a solution of this invention.

DETAILED DESCRIPTION

Referring to FIGS. 1-3, there is illustrated an electropolishing bath 10 which includes a tank 12 illustrated as having a rectangular parallelepiped configuration, but which can be cubic in its most efficient configura-

tion. The walls of the tank 12 can be fabricated from or lined with stainless steel sheet, polymer, glass laminates, polyvinyl chloride, or any other material which is relatively inert to chemical action by the electropolishing solution. Lead lined tanks can be used if the polishing solution is provided with additional Cu$^{2+}$ and Fe$^{3+}$ ions above that required as electrolyte.

A pair of cathode plates 14 and 16 are carried on insulated bearings 18, 18', and 20, 20', respectively, secured at the edges of the two opposite walls of the tank 12 so that the cathode rods 14 and 16 are disposed adjacent, but spaced from, the other two opposite walls of the tank 12. An anode bar 22 is carried centrally parallel to the cathode bars 14 and 16 by insulated bearings 24 and 24' secured to the top edges of the first mentioned opposite tank walls. A pair of cathode plates 26 and 28 are suspended from the cathode bars 14 and 16 by electrically conductive wire rods 30, 30', 32 and 32' and extend into the tank so as to occupy about 80--85% of the tank cross-sectional area. It is, of course, important that the cathodes be completely out of contact with the tank walls where stainless steel or other conductive metal is used for the walls. The cathodes 26 and 28 can be constructed of stainless steel or copper sheet, or other good electrical conductor.

The articles to be electropolished can be suspended directly from the anode bar 22 by conductive wire or rods hanging from the anode bar 22, or a rack 34, as illustrated, can be used. The rack 34, or suspension wire, can be formed of bare brass, copper, beryllium-copper alloy, aluminum, titanium, and the like. However, it is preferred that the rack or supporting wire have minimum exposure consistent with conductivity to the article to be polished. An appropriate rack can be formed of insulated copper or brass spleens with exposed titanium contacts 36 to hold the articles. The articles illustrated are steel cylinders 38, but the external surface of any article configuration can be electropolished. Where deep recesses in the article are present, auxiliary cathodes, bare or insulated in part, may be required since the internal "throw" for polishing is only approximately 75% of the recess diameter. In such case, selective chemical milling may be accomplished by a selectively bored auxiliary cathode appropriately disposed within the recess, all as known to the prior art.

A DC power supply 42 is connected so as to place a positive potential on the anode and negative potentials on the cathodes. While the total current drawn depends upon the type of rack and number of work pieces used, appropriate current densities for both polishing and chemical milling can be obtained with the solutions used herein, at about 8--12 volts DC. For reaction tanks up to approximately 500 gallons capacity, 1,000-ampere supply is generally adequate.

The tank 12 is filled with an electropolishing solution 40 so as to completely cover the cathode plates 26 and 28 and articles to be processed. The electropolishing solution is of a unique formulation for this purpose and imparts the advantages as hereinbefore described. In its fully operative condition, the electropolishing solution 40 contains 68.5--88.5 weight percent PO$_4^{3-}$, 0.001--0.01 weight percent of an oxidizing component selected from chromium sesquioxide and a trivalent titanium oxide, and a small amount of current supporting electrolyte. When the oxidizing component is chromium sesquioxide the bath has application to most industrial metals. It will clean and brighten magnesium,
selenium, plutonium, thorium, beryllium, uranium, halfnium, manganese, vanadium, columbium, silicon, gallium, iron, cadmium, indium, thallium, nickel, molybdenum, germanium, tungsten, zirconium and copper alloys including these metals, and will clean (but without marked brightening) zinc, cobalt, tin and lead. Generally, any metal which is capable of being oxidized by the reduction of trivalent chromium can be cleaned. Accordingly, a broad spectrum bath is provided by the utilization of chromium sesquioxide as the oxidizing component. A variety of metals can be processed simultaneously, such as stainless steel, aluminum, copper or brass. Successive use on other metals can be accomplished without interference or smudging by preventing polarization on the surfaces of the articles. On the other hand, the solution does not polarize on the ferrous metals, brass, copper, aluminum or aluminum alloys, and single replacement reaction may be accommodated by submerging and withdrawing the articles under power.

When it is desired to clean and brighten titanium and tantalum, one can utilize a trivalent titanium oxide as the oxidizing component. The trivalent titanium oxide can be used to clean or any metal capable of being oxidized by the reduction of trivalent titanium. The term "trivalent titanium oxide" is meant to include titanium sesquioxide and hydrates thereof. The titanium compound component can be added as such or produced in situ, and in this latter case the exact nature of the hydrate cannot be readily definitively ascertained.

The electropolishing solution 40 can be used initially with only the phosphoric acid and sesquioxide components, but preferably, divalent nickel is added directly or by oxidation from the cathode. The NiO acts as supporting electrolyte and, as a result of its favorable redox potential, enhances the electropolishing activity of the bath. When the solution in such form is used, metallic ions are oxidized from the surface of the articles into the solution and therefrom serve, not as contaminants, but as supporting electrolyte. The solution can thus derive its current bearing capabilities from the articles themselves, and it is found that large amounts of such ions can be accommodated in the solution and actually improve its performing characteristics. When large excesses of metal ions are present they either self-leach by precipitating out as insoluble sediments or reduce at the cathode, as cathode "sludge" and can therefrom be mechanically removed. Anionic impurities precipitate with the cations or, in the case of anions such as NO₃⁻, SO₄²⁻ or halogen, can be cleared by the addition of a metal carbonate. Importantly, it has been found that solutions loaded with impurities "recover" overnight and in the absence of the aforementioned anions has an indefinite useful life.

An anode of stainless steel is advantageously utilized to provide the divalent nickel ions. Trivalent iron ions and divalent copper ions are also leached into solution from articles as they are electropolished, as well as from racks and hangars, and serve as additional supporting electrolyte. The chromium sesquioxide or trivalent titanium oxide can also be leached from corresponding metal plates immersed in the phosphoric acid as anodes.

On the other hand, by relying upon the in-situ provision of components, the initial processing bath requires changes in operating parameters to accommodate the varying current capacity and electropolishing characteristic of the bath as it is being brought up to full strength. Accordingly, it is advantageous to initially add the sesquioxide and supporting electrolytes to the bath to immediately establish more uniform operating parameters. The components can be added in any form which will result in their dissolution in the phosphoric acid.

The phosphoric acid is used in sufficient concentration so that the electropolishing solution has a low vapor pressure, greatly minimizing its toxicity. It also serves as a means for suppressing and controlling H⁺ and OH⁻ ions as a precipitation bath for cations which have an insoluble phosphate, oxide or hydrate form or other insoluble form. The phosphoric acid is used in amounts ranging from about 68.5-88.5 weight percent. The chromium sesquioxide or trivalent titanium oxide, as above indicated, can be obtained from the pure metal by electrolytic decomposition in the phosphoric acid; or it may be added as such to the bath. At the above concentration levels of phosphoric acid, the electropolishing bath has a specific gravity of about 1.45-1.70. Too low a specific gravity may result in picking of the processed article. With too high a specific gravity, the temperature required for proper operation is so high as to cause excessive vapor pressure and attendant danger to the workers. A preferred specific gravity range is about 1.58-1.62 and at this range, the electropolishing bath can be advantageously operated at a temperature of about 135°F-145°F.

Divalent nickel can be added as a water slurry of nickelous carbonate. Generally, a minimum amount of 0.002 weight percent of divalent nickel ions can be used and it can be present to the extent of 0.2 weight percent of the ions, although even higher amounts can be accommodated. Iron ions will likely be an immediate contaminant which, in the absence of initial iron ions, may change the operating parameters of the bath. Accordingly, by adding trivalent iron initially these parameters can be present. The trivalent iron can be added as Fehd 2O₃ dissolved in phosphoric acid. Generally, an amount ranging from about 0.005 to about 0.05 weight percent or higher can be used. Copper can also be added as supportive electrolyte and can be added as cupric phosphate. Alternatively, by using a technical grade of ferric oxide, sufficient divalent copper may be present to provide the desired amount. Generally, an amount ranging from about 0.01 to about 1.5 weight percent, or higher, can be used. Any excess iron or copper will be plated onto the cathode as a loose sponge and can subsequently be removed by mechanical scrubbing or spray washing as hereinafore described.

Solutions formulated in accordance with the foregoing specification provide uniquely effective electropolishing and chemical milling baths. Referring to FIG. 4, a particularly unique advantage obtained by utilizing such baths is schematically illustrated wherein the surface of a metal object 44 processed through the bath is provided with a surface defined by a monomolecular layer 46 of oxide of the metal. The term "monomolecular" is meant to include both charged and uncharged molecules; i.e., the term includes monionic material. While it is not desired nor intended to be limited to any particular theory of operation, it appears that oxidation at the anodic surface of the processed article and liberation of oxygen does not occur solely from the conver-
sion of hydroxyl ion to hydrogen ion and oxygen, but also appears to result from an oxo or other negatively charged coordination complex anion associated with the active oxide and such mechanism may account for the monomolecular structure of the surface oxide layer of the article being processed. For example, using a solution of trivalent titanium oxide in the phosphoric acid with stainless steel (300 series) for both anode and cathode, the stainless steel was polished by metal removal at both electrodes, indicating the presence of both positive and negative ions capable of oxidizing the stainless steel (Cr, Ni) at both electrodes. The positive ion (attracted to the cathode) is capable of oxidizing titanium metal in the presence of H+ and H2O gas, and at the anode trivalent titanium oxide is formed along with the liberation of oxygen. Regardless of the mechanism of operation, metal articles polished with the electropolishing solution as described herein are brighter in appearance, are passivated against corrosion and have much greater resistance to smudging than articles processed with prior art solutions. Prior art processes result in the formation of multiple layers of metal oxide, providing adsorption and/or absorption centers for fingerprints and other smudges. However, the monomolecular surface of metal oxide provided by treatment with triphosphoric acid solution has insufficient depth to accommodate corroding particles or oil materials. This is particularly evident with copper and aluminum and alloys thereof.

Upon extended use of the solutions herein, cationic impurities will either precipitate out as insoluble sediments, be reduced at the cathodes as cathode sludge (removable by mechanical scrubbing), or contribute to ionic current support. Anionic impurities may precipitate with the cations and it has been observed that the solution recovers overnight when loaded with impurities. Following extensive processing of articles which have previously been passivated by treatment with nitric acid, NO3- (e.g., 50 ppm) may be present in excess which, unless removed, may cause pitting of stainless steel articles and should be removed. The solution can be cleared of such ions and of halogen and SO42- ions by the addition of a hot water slurry of nickelous carbonate or other metal carbonate to the solution. In the absence of NO3-, halogen, or SO42- ions the solution has an indefinite lifetime. Water can be lost by both evaporation and electrolysis. Phosphoric acid is primarily lost by drag-out and oxidation of organic materials introduced into the solution during processing of dirty parts. Thus, volume and specific gravity are simply adjusted by the addition of water and concentrated, e.g., 85 weight percent, phosphoric acid. When reconstituting to replace losses, a water solution of the sesquioxide oxidant can be added, decreasing the specific gravity, or phosphoric acid can be added to increase the specific gravity. As previously noted, if copper ion accumulates in high concentration (evidenced by a decrease in polishing efficiency), the excess ions can be readily removed by running stainless steel at the anodes and cathodes and removing the cathode sludge by mechanical scrubbing or spray washing.

The following examples in which all parts are by weight will illustrate aspects of the invention.

Example 1

An electropolishing and chemical milling solution was prepared having the following formulation:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>PO43-</td>
<td>78.5%</td>
</tr>
<tr>
<td>Ni2+</td>
<td>0.0038%</td>
</tr>
<tr>
<td>Cr2O3</td>
<td>0.0002%</td>
</tr>
<tr>
<td>Fe3+</td>
<td>0.0010%</td>
</tr>
<tr>
<td>Cu2+</td>
<td>0.03%</td>
</tr>
<tr>
<td>H2O</td>
<td>19.0</td>
</tr>
<tr>
<td>H2O2OH</td>
<td>balance</td>
</tr>
</tbody>
</table>

Initially 85% by weight of phosphoric acid was placed in the reaction tank and the required amount of Fe3+ was added as ferric oxide. The required amounts of Cu2+ and Ni2+ were added as cupric phosphate and as a water slurry of nickel carbonate, respectively. The required amount of chromium sesquioxide was added as such. The temperature was brought to 135°F-145°F and diluted with dionized water until a specific gravity of 1.58-1.62 was obtained.

A new stainless steel casting with a dull finish was placed in a rack, such as illustrated as 34 in FIGS. 1-3, in contact with the anode bar 32. About 5-10 volts DC were applied for about 12 minutes and the casting was removed and found to have a clean bright finish.

For comparison purposes, a similar stainless steel casting was processed in accordance with military specification MIL. S 5,002 wherein it was soaked in a hydrofluoric acid-nitric acid bath for one hour to passivate the surface. Upon removal from the processing bath, the casting had a clean, brightened surface but not as bright as obtained with only 12 minutes processing in the phosphoric acid-sesquioxide solution. The casting surface retained fingerprints to a much greater extent than the first sample. Both castings were exposed under similar conditions to salt spray for a period of 6 months after which they were inspected. It was found that the casting processed in accordance with the military specification was extensively corroded but the casting processed with the phosphoric acid-sesquioxide solution showed only minor evidence of corrosion.

Example 2

The phosphoric acid-chromium sesquioxide solution formulated in Example 1 was used to process metal articles formed of chromium, nickel, stainless steel, copper, brass, manganese, aluminum, zirconium, plain steel and cast iron and in each case was found to clean and brighten the article. The conditions were as described in Example 1 except that the average processing time was about 6 minutes.

Example 3

The phosphoric acid-chromium sesquioxide processing solution of Example 1 was used to process tin and zinc articles and was found to clean the articles, but with dull finishes.

Example 4

A phosphoric acid-sesquioxide bath was formulated in accordance with Example 1 but substituting titanium sesquioxide for the chromium sesquioxide. The bath was used to clean and brighten titanium, tantalum and cobalt articles.

Example 5

After extensive use of the phosphoric acid-chromium sesquioxide bath of Example 1, a loss of efficiency of process was noted by a lengthening of processing time required for brightening of metal parts. The solution
was allowed to remain overnight and upon its reuse was found to be restored to its original efficiency.

As required, detailed illustrative embodiments of the invention have been disclosed. However, it is to be understood that these embodiments merely exemplify the invention which may take forms different from the specific illustrative embodiments disclosed. Therefore, specific structural and functional details are not necessarily to be interpreted as limiting but as a basis for the claims which define the scope of the invention.

I claim:

1. A method for electropolishing a metal article utilizing:
   a tank;
   an electropolishing solution in said tank;
   at least one cathode in said solution;
   means for immersing a metal article to be electropolished in said solution;
   a power supply; and
   means for electrically connecting said cathode and metal article to said power supply;

said electropolishing solution comprising about 68.5–88.5 weight percent PO$_4$$^{3-}$, about 0.001–0.01 weight percent oxidizing component selected from chromium sesquioxide and a trivalent titanium oxide, about 0.0002–0.2 weight percent Ni$^{2+}$ and from about 0 to about 2 weight percent electrolyte selected from Fe$^{3+}$ and Cu$^{2+}$, the balance comprising essentially H$_2$O, H$_3$O$^+$ and OH$^-$.  

2. The invention according to claim 1 in which said solution has a specific gravity of about 1.45–1.70 and a temperature of about 115°F–1902°F.

3. The invention according to claim 1 in which said solution has a specific gravity of about 1.58–1.62 and a temperature of about 135°F–145°F.

4. The invention according to claim 1 in which said solution consists essentially of the following components in weight percentages;
   PO$_4$$^{3-}$ 68.5–88.5
   Cr$_2$O$_3$ 0.001–0.01

5. The invention according to claim 4 in which said solution includes about 0.0005–0.05 weight percent Fe$^{3+}$ ions.

6. The invention according to claim 4 in which said solution includes about 0.01–1.5 weight percent Cu$^{2+}$ ions.

7. The invention according to claim 4 in which said solution includes about 0.0005–0.05 weight percent Fe$^{3+}$ ions and about 0.01–1.5 weight percent Cu$^{2+}$ ions.

8. The invention according to claim 1 in which said solution consists essentially of the following components in weight percentages:
   PO$_4$$^{3-}$ 68.5–88.5
   Trivalent titanium oxide 0.001–0.01
   Ni$^{2+}$ 0.002–0.2
   Fe$^{3+}$, Cu$^{2+}$ 0–2
   H$_2$O, H$_3$O$^+$, OH$^-$ Balance

9. The invention according to claim 8 in which said solution includes about 0.0005–0.05 weight percent Fe$^{3+}$ ions.

10. The invention according to claim 8 in which said solution includes about 0.01–1.5 weight percent Cu$^{2+}$ ions.

11. The invention according to claim 8 in which said solution includes about 0.0005–0.05 weight percent Fe$^{3+}$ ions and about 0.01–1.5 weight percent Cu$^{2+}$ ions.

12. A method of reconstituting a used electropolishing solution formed of major amounts of phosphoric acid and minor amounts of chromium sesquioxide, said solution being contaminated with excess ions selected from ions of NO$_3^-$, a halogen and SO$_4^{2-}$ or combinations thereof, comprising adding a metal carbonate to said solution.

13. The invention according to claim 12 in which said metal carbonate is nickelous carbonate.
3. UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION


Inventor(s) Howard M. Greene

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 36, "contain" should be --contains--.
Column 4, line 22, "electrooolishing" should be --electropolishing--.
Column 4, line 41, "FeH2O" should be --Fe2O3--.
Column 6, line 18, before "34""as" should be --at--.
Column 6, line 24, "$5,002" should be --$5002--.
Column 7, line 32, "1902F" should be --190°F--.
Column 8, line 19, "Es" should be --Fe--.
Column 8, line 34, "contaminated" should be --contaminated--.

Signed and sealed this 17th day of September 1974.

(SEAL)
Attest:

McCoy M. Gibson Jr. C. Marshall Dann
Attesting Officer Commissioner of Patents