Improved cyanide-free aqueous electroplating baths for plating metals, the baths containing water soluble phosphonate chelating agents combined with at least one chelatable metal ion and containing as an additive at least one strong oxidizing agent, and electroplating processes employing said baths. Additional materials may also be added for further improvements.

3 Claims, No Drawings
This invention relates broadly to the electroplating of metals and metal alloys from cyanide-free aqueous plating baths. More specifically, this invention relates to improved cyanide-free aqueous electroplating baths containing a stable metal chelate formed from a water soluble phosphate chelating agent combined with at least one chelatable metal ion and containing as an additional additive at least one strong oxidizing agent. It is also contemplated to add certain other selected classes of materials to the improved baths in order to achieve further advantageous results.

It is one object of this invention to provide improvements in cyanide-free plating baths for electroplating metals.

It is another object to add strong oxidizing agents to electroplating baths to improve the brightness characteristics of the metal deposits therefrom.

It is a further object to improve the life of phosphate chelate-containing, cyanide-free electroplating baths by the addition thereto of at least one strong oxidizing agent and, as an additional feature, other property-improving additives.

Other and further objects of the invention will become apparent from the more detailed description of the invention set forth below.

Alkaline electroplating baths containing cyanides are widely used in industrial metal electroplating operations for the plating of certain metals. For many applications these cyanide-containing baths produce excellent results. The conventional electroplating baths consist essentially of aqueous alkaline solutions of the cyanide salt of the metal to be electroplated. In addition to these salts, additives may be included to improve the quality of the electro-deposits obtained therefrom. These additives can be used to produce grain refining, brightness, improve the bright plating range, or in general to impart desirable characteristics to the deposit or the operation of the bath. Typical examples of commonly employed additives are aromatic alkyl sulfonates which improve the luster of the plated metal surface and increase the uniformity of the plating baths to increase the amount of plating current density — and hence plating speed — which may be utilized without a roughening or “burning” of the plated surface. Further additives are employed to improve the “throwing power” of the electroplating bath, i.e., the ability of the bath to deposit a uniform thickness of plating metal in the recesses of a base metal object.

While excellent results can be obtained by using the above described cyanide-containing baths, the extreme toxicity of these solutions as the result of the presence of large quantities of cyanide presents disadvantages and makes their use undesirable. In addition to the inherent health hazards to personnel in the vicinity of the plating solution, a further problem is created by the need to destroy all of the cyanide before it is allowed to enter any stream or sewer system. The presence of even trace amounts of these chemicals in streams or sewers presents a severe health hazard and highly dangerous pollution problem. The chemical destruction of cyanides, on the other hand, is both cumbersome and expensive. Also, if the pH of an alkaline cyanide plating bath inadvertently becomes neutral or acidic, lethal hydrogen cyanide gas may form, creating a distinct hazard to all those in the vicinity.

Alkaline pyrophosphate electroplating baths are also in use today. These baths, however, have been found to be extremely sensitive to organic contamination and require periodic dilutions as the concentration of orthophosphate in the bath increases due to the hydrolysis of the pyrophosphate ion. Thus, the effective concentrations in the bath at any one time may be somewhat uncertain.

Attempts to overcome the difficulties described in cyanide electroplating and other above mentioned plating baths while retaining the advantages thereof have been made. For instance, electroplating solutions have been developed which contain a salt of the metal which is to be deposited and a phosphonic acid derivative as the chelating agent for the metal to be plated. Such plating solutions are described in French Pat. No. 1,458,492 to Monsanto Co. and in U.S. Pat. No. 3,474,293 to Haynes and Langguth assigned to Monsanto Co. as well as in pending U.S. application Ser. No. 825,076 of Nobel and Ostraw, assigned to Lea Konal, Inc., now abandoned. These patents describe electroplating baths containing a complex consisting of a divalent metal ion and an organophosphorous ligand of the formula:

\[
\text{Z} - \text{O}_n \text{OM}_m
\]

where \( n \) is an integer of from 2 to 3, \( n \) is a member selected from the group consisting of a hydrogen ion, ammonium, lower alkyl amine or an alkali metal cation and \( Z \) is a connecting radical equal in valence to \( n \) and containing not more than about 12 carbon atoms exclusive of hydrogen in chemical combination and is selected from the group consisting of (1) an aliphatic radical (2) an N-substituted aliphatic radical containing from 2 to 3 alkyl groups in which the connecting radical has a carbon atom linked to a phosphorus atom in the ligand.

In addition, polyamine phosphonate compounds are described in aforementioned U.S. Pat. application Ser. No. 825,076 in conjunction with electroplating baths containing in addition to the polyamine phosphonate, a chelatable metal ion.

Initially, the cyanide-free baths prepared in accordance with these improved processes of the prior art patents and the patent application aforementioned are semibright to lustrous. However, these so-called improved electroplating solutions are not commercially practicable because as the electroplating process proceeds, the metallic deposit tends to become continually duller and more granular, particularly in the low current density areas.

For example, 267 ml. of the following plating solution was prepared:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper metal as the hydroxide</td>
<td>180 g/l</td>
</tr>
<tr>
<td>Ethylenediamine tetramethylphosphonic acid</td>
<td>15 g/l</td>
</tr>
<tr>
<td>Potassium hydroxide</td>
<td>8 g/l</td>
</tr>
</tbody>
</table>

This solution was electrolyzed for 5 minutes at 1 ampere. The deposit was uniformly lustrous or semibright. However, continued electrolysis for an additional 120 ampere minutes (1 ampere for 120 minutes) the deposit became dull and granular, particularly
in the low current density areas. This plating solution is therefore entirely impractical for commercial electropainting operations, since it has very short life for producing satisfactory results in terms of the metallic films deposited thereon.

It has now been found that oxidizing agents may be used with the water soluble phosphonate chelating agents to alleviate the problem of poor luster. Their use results in a greatly improved deposit. In general it has been found that the stronger oxidizing agents such as the peroxides, chlorites, perchlorates, hypochlorites, permanganates, sulfites, and the like are most beneficial. In particular, it was found that chlorites are long lived as effective additives to the solutions and give superior results. The improvement caused by the addition and periodic replenishment of the oxidizing agents makes the chlorite containing bath a practical plating bath. Particularly useful compounds include:

- N-bromosuccinimide
- N-chlorosuccinimide
- Chloroperbenzoic acid
- Dimethyl sulfoxide
- Peroxide acid
- Permaleic acid
- Pyridine N-oxide
- Potassium peroxymonsulfate
- Ammonium persulfate
- Sodium or potassium perborate
- Sodium chloride
- Sodium hypochlorite
- Hydrogen peroxide
- Potassium permanganate
- Potassium perchlorate
- Potassium peroxydisulfate

Also useful are certain inorganic high energy oxidizers such as the fluoronitrogen compounds examples of which are nitrogren trifluoride, difluorodiazine, tetrafluorohydrazine, difluoramidine, chlorodifluoromaine, and fluorine and fluorohalogens compounds including chlorine trifluoride and derivatives, chlorine pentafluoride, chlorine fluoride oxides, oxygen fluorides and related compounds, and chlorine oxides and related compounds.

The amount of the selected oxidizing agent required varies somewhat with the particular oxidizing agent selected to be used and the amount of electrolysis the bath has undergone. Sufficient oxidizing agent is used to overcome the bad effects produced by continuation of electrolysis. The amount of sodium chloride, the preferred material, required is about 0.25 g/l in most baths. The range of use for the oxidizing agents is from about 0.01 g/l up to about 5 g/l, but in all cases the minimum amount necessary to produce good results should be employed. The amount required can readily be determined by a Hull cell test, which is a plating test cell used by all plating laboratories.

Examples of chelating agents which may be used as the basic ingredient of these baths include diethylenetriamine pentamethylenephosphonate acid, triethylenetetramine hexamethylenephosphonate acid, tetraethylenepentamine heptamethylenephosphonate acid and their alkali metal or ammonium salts. Further examples of useful chelating agents are ethylene diamine tetramethylenephosphonic acid, hexamethylene diamine tetramethylphosphonic acid, amonooxidyl ethanolamine trimethylphosphonic acid, aminooxidyl piperazine trimethylenephosphonic acid, diamino pyridine tetramethylenephosphonic acid, and their alkali metal or ammonium salts. Chelating agents also useful are hydrazine tetramethylenephosphonic and its alkali metal or ammonium salts.

In the hereinbefore described formula I for the organophosphorus ligand when Z is an aliphatic radical containing from one to 12 carbon atoms the ligand will preferably have the formula:

\[
\begin{align*}
N - (\text{X}) - (\text{Y}) - (\text{Z}) \\
\text{wherein X is selected from hydrogen, hydroxyl or a lower alky} \\
\text{group containing from one to about four carbon atoms and Y is a member selected from the group consisting of hydrogen, hydroxyl and lower alky} \\
\text{group containing from about one to about four carbon atoms, and M is as hereinbefore described.}
\end{align*}
\]

In the above formula I when Z is an N-substituted aliphatic connecting radical containing 3 alkyl groups the organophosphorus ligand will have the formula:

\[
\begin{align*}
N - (\text{X}) - (\text{Y}) - (\text{Z}) \\
\text{where X, Y and M are as hereinbefore described.}
\end{align*}
\]

Compounds falling within the scope of the foregoing general formula include aminotri(etheraline phosphonic acid) compounds and specific compounds falling therein include, for example, aminotri(methylene phosphonic acid), aminotri(ethylenediphosphate acid), aminotri(isopropylidene phosphonic acid), aminotri(methylene phosphonic acid), mono(ethylenediphosphate acid), aminotri(methylene phosphonic acid) mono(isopropylidene phosphonic acid), aminotri(methylene phosphonic acid) di(ethylenediphosphate acid), aminotri(methylene phosphonic acid) disopropylidene phosphonic acid and the like.

Lower alkylenediphosphonic acid compounds falling within the scope of the above general formula include methylene diphenosphonic acid, ethylenediphosphonic acid, isopropylidene diphenosphonic acid, 1-hydroxyethylidene diphenosphonic acid, 1-hydroxypropylidene diphenosphonic acid, butylenediphosphonic acid and the like.

As stated hereinbefore M in the above formula may be among others, a hydrogen ion or an alkali metal cation. It is preferred that M be an alkali metal cation such as sodium, potassium and lithium.

Particularly preferred organophosphorus ligands employed in the form of a divalent transitional metal ion complex include for example, pentapotassium amino(trimethylene phosphonate), tetrapotassium 1-hydroxyethylidene diphenosphonate, pentasodium aminotri(methylene phosphonate), tetrasodium 1-hydroxyethylidene diphenosphonate.

The plating bath of the present invention may be prepared for instance by forming an aqueous solution of a suitable metal compound and a phosphate chelating agent of the present invention. Another method for preparing the baths disclosed herein is to form an aqueous mixture of a metal chelate salt which has been previously prepared, e.g., by the reaction of a chelatable metal carbonate, hydroxide or oxide with a phosphonic acid of the present invention, then neutralizing and adjusting the pH with a suitable alkaline compound such as sodium hydroxide, potassium hydroxide, ammonium hydroxide, or the alkali metal carbonates.

The oxidizing agent of the invention is then added in the required small but effective concentration quantity.
It may be added initially or only after the bath has reached a stage in which it is not producing a satisfactory bright deposit.

Any water soluble metal compound which will form chelates with the above-described chelating agents may be used for the plating solutions of this invention including soluble compounds of iron, cobalt, nickel, zinc, silver, copper, cadmium and tin. The metal compounds employed in making up the baths may be (1) ionic metal salts which when solubilized release a chelatable metal ion, e.g., copper sulfate, or (2) complex salts which, when solubilized, will supply a chelatable metal ion, e.g., sodium zincate, or (3) metal salts, such as the carbonates which will react with phosphonic acid chelating agent to form a metal chelate salt. The plating of alloys can be achieved by the invention through the use of two or more different chelatable metals in the proper proportions. Examples of alloys which have been plated by the present invention are copper-nickel alloy, and copper-zinc "yellow brass" alloy and copper-zinc "white brass" alloy.

For best results, essentially neutral electroplating solution of 6 to 9 pH is preferable, but higher pH ranges, up to 13 as well as lower ranges to about 3 or 4 can also be used.

A number of other and further features have been discovered as improvements in the invention. These generally are selected metallic and non-metallic ions and organic compounds which can be added to improve further the brightness obtained.

For example, it has been discovered that certain metal additives, when added to the plating baths of the invention, improve significantly the brightness of the deposits, provided the bath is stabilized with the oxidizing agent. These metals are thallium, lead and cadmium. The amounts used is about 0.01 to 0.5 g/l or a sufficient amount to give the brightness desired. These metals may be added as the soluble metal salt such as sulfate, acetate, tartrate, citrate, chloride, and the like. Other metallic ions which can also be used include arsenic, antimony and bismuth and the amounts used are about 0.01 to 1 g/l or a sufficient amount to give the brightness desired. The ions can be added as the soluble salt such as tartrate. Of the metallics above listed bismuth has been found to be preferred.

It has also been found that selenium and tellurium can be advantageously used in the stabilized bath. They may be added as the sodium selenite or tellurite. The amounts that are useful are about 0.1 g/l or an amount sufficient to improve brightness.

It has also been found that amino acids can be used to improve the brightness of metallic deposits. Amino acids that are useful as additives to the plating baths are lysine hydrochloride, cysteine hydrochloride, alanine, methionine, glycine, 1-tirosine, and the like. The preferred amino acid additive is glycine. The amount required is about 0.01 to 5 g/l or an amount sufficient to produce the desired effect. Amino acids increase the ability of the plating solution to withstand prolonged electrolysis without plating dull.

It has been found that metal additives can be used with the amino acids, i.e., bismuth ions with glycine with achievement of good results.

In order to illustrate the novel electroplating baths of this invention a series of baths are exemplified below. While particular embodiments of the invention are specifically shown, it will be understood that the invention is obviously subject to variations and modifications without departing from its broader aspects.

The plating baths were prepared by dissolving in water the indicated quantity of the compound of the metal to be electrodeposited and the indicated phosphate chelating agent. An alkali metal hydroxide was added to the solution to adjust the pH to the selected value. The examples illustrate the different metal compounds which can be used in the invention and which when solubilized release a metallic ion. For each of the baths described below, the electroplating of the metal was conducted in a 267 ml Hull cell, in a conventional manner at a temperature in the range of from room temperature to 140°F, and at a current of 1 amper. Various brighteners which are described as further features of this invention were added to the bath as specific embodiments of the invention.

**BATH A**

| Ethylenediamine tetramethyl-phosphonic acid | 120 |
| Copper sulfate | 60 |

The pH of the mixture was adjusted to 10.3 with potassium hydroxide. The electroplating was conducted at 140°F. The resulting copper deposit was of overall dull appearance with a burned portion in the high current area.

**BATH B**

| Ethylenediamine tetramethyl-phosphonic acid | 120 |
| Copper sulfate | 60 |
| Glycine | 4 |

This is Bath A with glycine added. One half the panel from the low current density is bright.

**BATH C**

| Ethylenediamine tetramethyl-phosphonic acid | 120 |
| Copper sulfate | 60 |
| Sodium selenite | 0.02 |

The pH of the mixture was adjusted to 8.0 with potassium hydroxide and the deposition temperature was 140°F. The copper deposit was uniformly bright with a narrow burn in the high current area.

**BATH D**

| 1-Hydroxymethylidyne-diphosphonic acid | 180 |
| Copper hydroxide | 24 |
| Cysteine hydrochloride | 0.04 |

Potassium hydroxide was used to adjust the pH to 10.3 and the metal was deposited at a temperature of
140°F. The resulting deposit was completely bright except at the high current area.

**BATH E**

<table>
<thead>
<tr>
<th>Grams per liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Hydroxyethylidene-diphosphonic acid</td>
</tr>
<tr>
<td>Copper hydroxide</td>
</tr>
<tr>
<td>Sodium bismuth tartrate</td>
</tr>
</tbody>
</table>

The pH was adjusted to 10.3 with sodium hydroxide and the temperature was 140°F. The resulting deposit was completely bright except in the area of high current.

**BATH F**

To Bath E there was added 2 g/l of glycine. The overall brightness of the metal deposited was improved.

**BATH G**

<table>
<thead>
<tr>
<th>Grams per liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Hydroxyethylidene diphosphonic acid</td>
</tr>
<tr>
<td>Copper hydroxide</td>
</tr>
<tr>
<td>Ethylenediamine tetramethyl</td>
</tr>
<tr>
<td>Phosphonic acid</td>
</tr>
</tbody>
</table>

The pH was adjusted to a pH of 10.3 with potassium hydroxide. The temperature used was 140°F. The resulting deposit was uniformly semibright; however, after electrolysis for 120 ampere minutes, the deposit became dull and granular.

**BATH H**

After the deposit became dull and granular, 0.5 g/l of sodium chlorite was added to Bath G. The deposit remained uniformly semibright throughout the entire period of electrolysis.

**BATH I**

After the deposit became dull and granular, 1 cc/l of dimethyl sulfoxide was added to Bath G. The deposit remained uniformly semibright throughout the entire period of electrolysis.

**BATH J**

<table>
<thead>
<tr>
<th>Grams per liter</th>
</tr>
</thead>
</table>

Potassium hydroxide was added to adjust the pH to 5.0. A temperature of 140°F. was used and the metal deposit was uniformly bright even after electrolyzing for 180 ampere minutes.

**BATH K**

To Bath G there was added 1 cc/l of 30 percent hydrogen peroxide. A metal deposit of uniform brightness was obtained throughout the entire period of electrolysis.

**BATH L**

To Bath G there was added 0.5 g/l of potassium permanganate. Good results in brightness were obtained throughout the entire period of electrolysis.

**BATH M**

8 ml/l of 7% sodium hypochlorite solution was added to Bath G. Similar good results were obtained with metal electrodeposition.

The above data demonstrate that the addition of oxidizing agents to the plating baths led to markedly improved deposition results.

What is claimed is:

1. In a process for producing deposits of metal which comprises electrodepositing metal from a cyanide-free aqueous solution containing an effective amount of a complex formed of a water soluble phosphonate chelating agent and at least one chelatable metal ion of a metal to be electrodeposited and capable of producing electrodeposits, the improvement which comprises including in the electroplating solution from about 0.01 to about 5.0 g/l of at least one oxidizing agent selected from the group consisting of peroxides, chlorites, perchlorates, hypochlorites, permanganates and sulfoxides.

2. The process according to claim 1 in which the metal undergoing electrodeposition is selected from the group consisting of iron, cobalt, nickel, zinc, silver, copper, cadmium and tin.

3. The process of claim 2 in which the metal undergoing electrodeposition is copper.