(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
17 February 2005 (17.02.2005)

PCT

(10) International Publication Number
WO 2005/014890 A1

(51) International Patent Classification[7]: C25D 3/02, 5/48, 5/10

(21) International Application Number: PCT/GB2003/003160

(22) International Filing Date: 23 July 2003 (23.07.2003)

(25) Filing Language: English

(26) Publication Language: English

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(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:

— *as to non-prejudicial disclosures or exceptions to lack of novelty (Rule 4.17(v)) for all designations*

Published:

— *with international search report*

— *with a declaration as to non-prejudicial disclosures or exceptions to lack of novelty*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: AN ELECTROLYTE SOLUTION

(57) Abstract: An electrolyte solution comprising at least one plateable metal ion capable of being reduced to the metallic form, at least one transition metal ion species, and a solvent, in which a passivated coating of the at least one plateable metal ion can be deposited on an article.

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An Electrolyte Solution

The present invention relates to an electrolyte solution and process that furnishes passivated metal coatings to substrate materials, and to articles treated using the same solution and process.

Electroplating solutions and processes are extensively employed to electrodeposit metallic coatings to substrates such as steels. Such coatings are used to afford desirable properties to the substrate material; for example, corrosion resistance, decorative finish, or wear resistance.

Established metallic coatings include cadmium, chromium, cobalt, copper, nickel, tin, silver, and gold. Other known coatings include iron, manganese, platinum, rhodium, and indium. Where sacrificial corrosion resistance is required, zinc is often the preferred choice. Zinc can be electrodeposited either alone, or in combination with other metals to form alloy coatings, for example, zinc-cobalt alloys, zinc-iron alloys, and zinc-nickel alloys.

Electrolytes currently used for plating purposes comprise various chemical species that serve one or more of the following functions: to provide a source of the metal or metals being deposited, to form complexes with ions of the depositing metal, to provide conductivity, to stabilise the solution e.g. against hydrolysis, to act as a buffer, to modify or regulate the physical form of the deposit, to aid in dissolving anodes, or to modify specific properties either of the solution or the deposit.

For example purposes only, a typical electrolyte used to deposit zinc might comprise zinc chloride as the source of the metal ions, ammonium chloride to provide conductivity, a buffer such as boric acid to regulate acidity, a detergent to prevent pores from forming in the deposit, and organic agents such as chlorobenzaldehyde to encourage the formation of bright and reflective coatings. Other additives, known as levelling agents, may be employed to promote the formation of flat electrodeposits that are free of dendrites. There are many other types of zinc electrolyte, including alkaline solutions that use cyanide salts for conductivity, and alkaline solutions that are free of cyanides.

Acidic zinc electrolytes may also contain nickel, cobalt, iron, or tin salts. These metals are often added as chlorides or sulphates. Such electrolytes are routinely used to deposit alloy coatings, namely, zinc-nickel alloys, zinc-cobalt alloys, zinc-iron alloys or zinc-tin alloys. These are more corrosion resistant than zinc alone. Alkaline solutions can also be used to produce similar alloy coatings provided complexing agents are added to the electrolytes partly in order to maintain selected metal ions in solution. Other metals such as tin and copper can be alloyed with dissimilar metals using the same principles. Examples include tin-lead, tin-bismuth, tin-nickel, copper-zinc, and copper-tin.

Before an article can be electroplated it must be thoroughly cleaned, lest the coating fail to adhere to the substrate or be of poor quality. Various proprietary cleaning agents and techniques are widely available, and include grit blasting, other types of blasting, solvent

include grit blasting, other types of blasting, solvent degreasing, aqueous cleaners, and a range of other methods.

An electroplating cell comprises the electrolyte, an anode material, and the article to be plated, which is the cathode. The anode and cathode are connected to an external power supply, and electricity is passed through the cell. The metal ions in the electrolyte are reduced at the cathode to form the desired metal coating. Following electroplating, the freshly coated article is rinsed several times to remove all traces of the electroplating solution. Suitable anode materials include blocks of the metal to be plated, titanium alloys, stainless steels, and a wide variety of other materials that are commercially available. Electroplating cells include vats, barrels, or those employed for continuous strip plating. Commercial electrolytes are supplied with detailed instructions on their preparation and use, and the recommended type of plating equipment.

In many instances, the electrodeposited coating does not possess the range of properties required for the intended application. By way of example only, electrodeposited zinc coatings tend to react with moisture in the air and forms loose corrosion products that are unsightly and prevent the adhesion of paints. For some applications, the coatings are also insufficiently decorative or lack adequate corrosion resistance. These problems are also encountered with other deposits such as the range of zinc alloys, and a variety of other metal coatings.

The above problems are usually overcome through the application of a chromate passivation film. The freshly deposited and rinsed coating may first be treated in several other solutions, such as an acid solution, rinsed again, and then immersed or otherwise brought into a solution of hexavalent chromate. The chromate solution then reacts with the surface of the coated article to form the passivation film.

Chromate passivation films impart many beneficial properties, including a decorative finish, additional corrosion resistance, and provide an excellent surface for paints. Chromates can also provide a range of coloured finishes to sometimes quite dull and unattractive coatings, including iridescent, yellow, green, blue, olive drab, and black. They also remove hazes and polish the coating surface to a bright and reflective finish. Chromate passivation films are commercially and routinely applied to a wide range of electrodeposited coatings, including aluminium, cadmium, copper, tin, zinc, and a wide range of alloy coatings, including the range of zinc alloys. Chromates have been in use for over sixty years and extensive ranges of proprietary formulations are commercially available.

Following the application of the chromate passivation film, the article is rinsed several times in water to remove all traces of hexavalent chromium, and the treatment process is concluded by drying the article, often in a stream of warm air.

The electroplating of an article followed by the application of a chromate passivation film is an established practice in the art, there are however

inherent drawbacks with this practice. The rinse water used to rinse the article following electroplating becomes contaminated with the electrolyte and eventually requires treatment. By way of example only, if a cyanide zinc electrolyte were used, the rinse water becomes contaminated with cyanide. The cyanide then requires reduction through chemical additions, which produce a precipitate, followed by filtration to remove the solid matter, and subsequent disposal, often to a landfill site. The water left over from this treatment process may require subsequent treatment, for example, through the use of ion exchange columns, to render the water sufficiently pure for reuse or disposal.

Other problems relate to the use of hexavalent chromates. The rinse water used to remove all traces of hexavalent chromium becomes contaminated with hexavalent chromate ions. The treatment of this contaminated rinse water is problematical due to the toxicity and carcinogenic nature of hexavalent chromate. Chromates are also toxic to the environment, and a threat to the health and safety of the workforce. There are also mounting concerns over the handling and disposal of chromated components and parts. Consequently, many countries around the world are taking action to reduce or ban the use of chromates.

The chromate contaminated rinse water is treated in several different ways. One approach is to make chemical additions to convert the hexavalent chromium to the less harmful trivalent chromium. A precipitate of the trivalent chromium is produced that is then filtered into a solid cake before disposal to landfill. The water left over may be evaporated in concrete trenches or subject to

further treatment to remove the remaining traces of chromate, for example, by ion exchange chromatography. The treated water may then be reused or sent to drain. The ion exchange columns need periodic regeneration, and the chromium-contaminated resins require additional special treatment.

Current electroplating processes thus often comprise not only of the electroplating stage itself, but numerous rinses and other chemical treatments, and the use of toxic and carcinogenic chromates. Alongside the actual treatment stages, a great deal of equipment is required to handle and treat toxic and dangerous waste. The numerous tanks, vats, and other vessels, occupy a large amount of factory space. The treatment solutions and associated equipment such as pumps and heaters consume a great deal of electricity, and the many rinse stages demand the use of extremely large volumes of water. The generation of toxic waste often requires the use of landfill, which is expensive and environmentally undesirable.

The plating industry has made attempts to improve the efficiency of the individual treatment stages, and in the introduction of better waste treatment. However, the fundamental problems associated with complicated multi-stage plating processes remain, namely heavy consumption of resources such as water and electricity. In addition, there are currently no viable alternatives to the use of chromate passivation films, and hence a serious health and environmental hazard remains in widespread use.

It is an aim of the present invention to provide an electroplating solution that furnishes both a metal

coating and a chromate-free passivation film from the same solution, eliminating the need for multiple stage treatment processes and no toxic substances are employed.

Accordingly a first aspect of the present invention is directed to an electrolyte solution comprising at least one plateable metal ion capable of being reduced to the metallic form, at least one transition metal ion species, and a solvent, in which a passivated coating of the at least one plateable metal ion can be deposited on an article.

Accordingly a second aspect of the present invention is directed to a process for coating a substrate comprises contacting an article with a solution which comprises at least one plateable metal ion capable of being reduced to the metallic form, at least one transition metal ion species, and a solvent; and in which the article forms the cathode of an electrochemical cell, passing a current through the electrochemical cell such that the at least one plateable metal ion is electrodeposited on the article, lowering or turning off the current passing through the electrochemical cell such that the electrodeposition of the at least one plateable metal ion is substantially stopped, leaving the electrodeposited coating of the at least one plateable metal ion in contact with the solution such that the at least one transition metal ion species forms a passivation film on the coating of the at least one plateable metal ion.

Accordingly a third aspect of the present invention is directed to a process for coating a substrate comprises contacting an article with a solution which

comprises at least one plateable metal ion capable of being reduced to the metallic form, at least one transition metal ion species, and a solvent; and in which the article forms the cathode of an electrochemical cell, comprising the steps of (a) passing a current through the electrochemical cell such that the at least one plateable metal ion is electrodeposited on the article, lowering or turning off the current passing through the electrochemical cell such that the electrodeposition of the at least one plateable metal ion is substantially stopped; followed by (b) leaving the electrodeposited coating of the at least one plateable metal ion in contact with the solution such that the at least one transition metal ion species forms a passivation film on the coating of the at least one plateable metal ion; wherein (a) and (b) are repeated any number of times, and in any order, to form a multi-layer coating comprising alternate layers of a coating of the at least one plateable metal ion and the passivation film formed from the at least one transition metal ion complex species.

The term 'plateable metal ion' refers to those metals widely known in the art that are capable of being reduced from their ionic form to their metallic form, usually on the passage of electrical current.

The electrodeposited coatings produced by the present invention are more corrosion resistant that those produced conventionally, and, since the passivation films are formed without the electrodeposit being exposed to the atmosphere, they are bonded into the coating at a molecular level, giving excellent properties such as adhesion, and the aforementioned corrosion resistance.

In addition, another feature is the capability to produce multi-layer coatings comprising alternate layers of electrodeposited coating and passivation film, which are coatings that cannot be produced by previously proposed methods.

Preferably, the at least one plateable metal ion is selected from: Ag^{+}, Au^{+}, Au^{3+}, Bi^{3+} Cd^{2+}, Co^{2+}, Cr^{3+}, Cr^{6+}, Cu^{+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, In^{+}, In^{3+}, Mn^{2+}, Mn^{3+}, Mn^{4+}, Ni^{2+}, Pb^{2+}, Pb^{4+}, Pd^{2+}, Pt^{2+}, Rh^{2+}, Rh^{3+}, Sn^{2+}, Sn^{3+}, Sn^{4+}, Sb^{3+}, Sb^{4+}, Sb^{5+}, Zn^{2+}.

Preferably, the at least one plateable metal ion is selected from: Ag^{+}, Co^{2+}, Cu^{+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Mn^{3+}, Mn^{4+}, Ni^{2+}, Sn^{2+}, Zn^{2+}.

Advantageously the counter ion to the at least one plateable metal ion may comprise any ion that gives rise to a salt of sufficient solubility in the chosen solvent.

The concentration of the salt or salts comprising the at least one plateable metal will preferably be in a range of 0.1 to 500g/L however higher or lower concentrations than this range may also be used as required.

Preferably, the at least one transition metal ion complex species is formed from reaction in solution between at least one transition metal ion species and at least one film forming agent.

Advantageously, the at least one transition metal ion species is a suitable species of at least one metal from the transition metal block of the periodic table.

Preferably, the at least one transition metal ion species is chosen from: Ti^{2+}, Ti^{3+}, Ti^{4+}, V^{5+}, V^{4+}, V^{3+}, V^{2+}, Zr^{2+}, Zr^{3+}, Zr^{4+}, Nb^{5+}, Nb^{4+}, Nb^{3+}, Nb^{2+}, Mo^{6+}, Mo^{5+}, Mo^{4+}, Mo^{3+}, Mo^{2+}, Hf^{2+}, Hf^{3+}, Hf^{4+}, Ta^{5+}, Ta^{4+}, Ta^{3+}, Ta^{2+}, Re^{7+}, W^{6+}, W^{5+}, W^{4+}, W^{3+}, W^{2+}, Mn^{6+}.

Advantageously, the at least one transition metal ion species is an oxide or halide moiety of the at least one transition metal ion species, chosen from: TiO_3^{2-}, $Ti_3Cl_{12}^{3-}$, TiO_5^{6-}, $Ti_2O_7^{6-}$, $Ti_6O_{13}^{2-}$, TiF_6^{2-}, $Ti_3O_7^{2-}$, $Ti_5O_{16}^{12-}$, ZrO_3^{2-}, $Zr_3O_{12}^{12-}$, ZrO^{2-}, ZrF_6^{2-}, ZrO_9^{2-}, HfO^{2-}, HfF_6^{2-}, VO_3^-, VO_4^{3-}, $Nb_2O_6^{2-}$, $Nb_5O_{15}^{5-}$, NbF_7^{2-}, NbO_3^-, TaF_7^{2-}, TaO_3^-, $Ta_2O_6^{2-}$, MoO_4^{2-}, $Mo_3O_{12}^{6-}$, WO_4^{2-}, $W_4O_{16}^{8-}$, $W_3O_{12}^{6-}$, MnO_4^-, ReO_4^-.

Preferably, the at least one transition metal ion species is an oxide moiety of the at least one transition metal ion species, chosen from: VO_3^-, VO_4^{3-}, MoO_4^{2-}, WO_4^{2-}, MnO_4^-.

Advantageously, MoO_4^{2-} and WO_4^{2-} are employed in the same solution.

Preferably when employed in the same solution the MoO_4^{2-} concentration is in the range 0.2 to 0.4g/L and the WO_4^{2-} concentration is in the range 0.8 to 1.2g/L.

Advantageously, when employed in the same solution the MoO_4^{2-} concentration is 0.2g/L and the WO_4^{2-} concentration is 0.8g/L.

Advantageously the counter ion to the at least one transition metal ion species may comprise any cation that gives rise to a sufficiently soluble salt.

Trace amounts of the salt or salts comprising the at least one transition metal ion species may be suitable. Preferably, the concentration range of the salt or salts comprising the at least one transition metal ion species is 0.01 to 100g/L, and especially the range is 0.1 to 10g/L. However, concentrations outside these ranges may also be suitable as required.

Preferably, the at least one film forming agent is a species that is capable of reacting with the at least one transition metal ion species to form a complex of the at least one transition metal ion species such that the complex is furnished with film forming properties.

Preferably, the at least one film forming agent is chosen from: ClO_4^-, $Cl_2O_2^{2-}$, NO_2^-, NO_3^-, PO_4^{3-}, SO_3^{2-}, $S_4O_6^{2-}$, IO_3^-, IO_4^-, $O2^{2-}$, $(OOH)^-$, $(H2OOH)^+$, $P_2O_8^{4-}$, $S_2O_6^{2-}$, $S_2O_8^{2-}$, $C_2O_4^{2-}$, ascorbic acid, tartaric acid or salicyclic acid.

Advantageously, the at least one film forming agent is chosen from: $S_2O_8^{2-}$ O_2^{2-}, IO_3^-.

Preferably the counter ion to the at least one film forming agent may comprise any cation that gives rise to a sufficiently soluble salt.

Trace amounts of the salt or salts comprising the at least one film forming agent may be suitable. Preferably, the concentration range of the salt or salts comprising the at least one transition metal ion species is 0.01 to 1000g/L, and especially the range is 0.8 to 10g/L. However, concentrations outside these ranges may also be suitable as required.

Preferably, the solvent is acidic, neutral, or alkaline

Advantageously, the solvent is water

Preferably, the solution further comprises a surfactant.

The surfactant minimises pore formation during electroplating. Suitable examples are known in the art and include sodium lauryl sulphate.

Preferably, the solution further comprises a conductivity salt.

The salt should provide satisfactory conductivity. Examples of suitable salts include ammonium chloride, sodium chloride, aluminium sulphate, and sodium hydroxide, others will readily occur to a man skilled in the art.

Preferably, the solution further comprises a buffer.

The buffer should stabilise the solution pH. An example of a buffer is boric acid, other suitable compounds will readily occur to a man skilled in the art.

Preferably, the solution further comprises a levelling agent.

The levelling agent should promote the formation of deposits with even thickness. Suitable salts will be known to those skilled in the art. Examples of levelling

agents include liquorice, glucose, saccharin, and ascorbic acid, other suitable compounds will readily occur to a man skilled in the art.

Preferably, the solution further comprises a brightening agent.

The chemical passivation films provide the coatings deposited using the solution and process with a bright, reflective, and smooth finish. In some instances, however, it may be desirable to further improve brightness. Suitable brightening additives will be known to those skilled in the art.

Preferably, the solution further comprises a complexing agent.

The complexing agent typically maintains the at least one plateable metal ion in acidic or alkaline solutions. Suitable complexing agents will be known to those skilled in the art.

The electrolyte solution according to the present invention is suitable for carrying out repeated electroplating operations. Chemical addition make-up is conducted in accordance with standard procedures, as will be known to those skilled in the art.

The process of the present invention is suitable for use with any form of electroplating equipment, for example, vats, barrels, selective plating, or continuous strip plating.

Advantageously the process for the present invention incorporates solution agitation.

Advantageously the process for the present invention incorporates cathode movement.

Advantageously the process for the present invention incorporates both solution agitation and cathode movement.

Examples of processes in accordance with present invention will now be described with reference to the accompanying drawings, in which:

Figure 1 shows a schematic diagram of a conventional plating process, and a schematic diagram of a passivated coating formed using the process;

Figure 2 shows a schematic diagram of a process according to the present invention, and a schematic diagram of the formation of a passivated coating using the process;

Figure 3 shows a current-time profile suitable for use in the process of the present invention to form a coating of the type shown in Fig. 2;

Figure 4 shows a current-time profile suitable for use in the process of the present invention to form a multi-layer coating, and a schematic of the formation of a multi-layer coating according to the process;

Figure 5 shows a current-time profile of a process according to the present invention and schematic diagrams of a passivated coating formed using the process; and

Figure 6 shows a suitable arrangement for solution agitation according to the present invention.

Figure 1 shows a conventional plating process with each box representing a separate stage wherein cleaned articles 2 are typically immersed in the electroplating solution 1 and the desired coating 3 is deposited onto the article from the plating solution.

The coated article is then moved through a sequence of rinsing and treatment stages 4 producing rinse water contaminated with plating solution, acid residues, and other many other different chemical species as waste that requires careful handling and treatment.

The coated article is transferred to the hexavalent chromate bath. This produces a chromate passivation film on the electrodeposited coating layer 5. Further rinsing concludes the treatment process and generates chromate-contaminated wastewater, which then requires extensive and expensive treatment.

Figure 2 shows a process in accordance with the present invention. The cleaned article 2 is transferred into the solution 6 and the electrodeposition and chemical passivation stages are carried out from the same solution 6. The article is thus furnished with both the coating layer 7 and passivation film 8 in a single treatment. The coated and passivated article is then

rinsed in water to remove residual amounts of the solution. The rinse water contains no dangerous or toxic substances, since no chromates are employed. The rinse water may be treated with standard metal recovery methods such as ion exchange, reverse osmosis, or electrodialysis, and hence recycled 9.

A comparison with Figure 1 shows that for the typical example shown, the present invention eliminates five water rinse stages, a neutralising rinse, an acid rinse 4, and the chromate treatment. The present invention thus greatly reduces the consumption of water and electricity, since far less solution requires heating, and also uses much less space for plating vessels, tanks, and other equipment. In addition, toxic chromates are eliminated, thus greatly simplifying waste treatment.

Figure 3 shows a process in accordance with the present invention, expressed as a current-time chart. A current 10 is applied to an article 2 and the metal ions that form the coating are reduced on the cathode to the metallic form to provide the coating layer 7. The value of the currents required for electrodeposition purposes will be known to those skilled in the art, and depend partly on the metal or metals of interest. Typical current densities range between $0.1A/dm^2$ and $10A/dm^2$, however, values outside of this range may also be suitable. For some metal ions it may be desirable or necessary to vary the current during the electrodeposition stage.

After a sufficient amount of current 10 has been passed to achieve the required deposit thickness, one

option is to turn off the current 11 at this point the article 2 is plated with the coating 7. The coated article remains in contact with the solution for a period 12 and it is during this period 12 that the passivation film 8 is formed.

Figure 4 shows another example of a process in accordance with the present invention wherein a current flow is not reduced to zero during passivation. As before, a sufficient current is passed through the plating cell to permit the reduction of metal ions to form the desired coating 10. During this period, the cathode voltage 13 will be at or below the reduction potential 14 required for the deposition of the metal ions. These terminologies and principles will be known to those practised in the art. At the end of the plating period the current is reduced 11 such that the cathode voltage shifts to a value that is nobler than the reduction potential of the metal ions involved 15. If necessary, the cathode potential can be measured using a commercially available reference electrode. When the passivation film has been formed over the required period, the treated article is removed from the solution.

Figure 5 shows an example of a process in accordance with the present invention for the formation of multi-layered coatings comprising of alternate layers of electrodeposited coating and passivation film. These coating systems possess a range of properties, including exceptionally high corrosion resistance, partly since the coatings contain in-built passivation films that act to suppress corrosive attack.

The first cycle shows the application of current 10 to permit electrodeposition. This forms the coating 7 on the substrate 2. The current is then turned off 11 and the passivation period 12 commences. During this time, the passivation film 8 is formed on the electrodeposited layer.

The second cycle begins immediately at the end of the first cycle, and current re-applied. This produces an electrodeposited layer 16 on the passivation film 8. The passivation stage of the second cycle generates a passivation film 17 on the underlying electrodeposited coating. The passivation film formed during cycle 1 thus becomes an interlayer between two electrodeposited coating layers.

The third cycle is then carried out, and this produces an article furnished with six layers of alternating electrodeposited coating and passivation film 18.

The three cycles are shown only for illustrative purposes and any number of successive cycles can be performed. The length of time over which either the electrodeposited coating or passivation filmed are formed can be varied such that the cycles times can be adjusted for a particular application. During the passivation stages, the technique illustrated by Figure 4 may also be employed if desired.

Figure 6 shows a plating cell 21 containing a solution 22. Four circulation pumps 23 are positioned within the cell 21. The pumps 23 are configured such that the movement of the solution 22 that subsequently

arises from their operation is such that the solution is directed towards the walls of the plating cell, shown by arrows 24. The resulting turbulence produces gentle agitation around the sample to be plated 25. By way of example only a distance of 3m between the pumps and 1m from the mid point between the pumps is shown. Suitable alternative configurations and agitation methods may be employed as appropriate.

Example 1.

A water solution comprised 60g/L zinc chloride, $ZnCl_2$, 100g/L ammonium chloride, NH_4Cl, 1g/L sodium molybdate, Na_2MoO_4, 1g/L ammonium peroxodisulphate $(NH_4)_2S_2O_8$, and 1g/L sodium lauryl sulphate surfactant.

The solution was maintained at 20°C. Commercial grade zinc anodes were used. A mild steel article was immersed in the solution and electroplating carried out at $1A/dm^2$ for 20 minutes, which was sufficient to provide a zinc deposit of approximately 10μm. The current was turned off, and the coated article permitted to remain immersed in the solution for a further 2 minutes, during which time the passivation film was observed to form on the coating surface.

The resulting passivation film was blue in colour, with a bright reflective appearance.

Example 2

The solution and process described in Example 1 was repeated, however, on this occasion the time period over which passivation was carried out was 8 minutes, as

opposed to 2 minutes. The 8-minute passivation period resulted in the formation of a bright yellow passivation film.

Example 3

The solution and process described in Example 1 was repeated, however, on this occasion the time period over which passivation was carried out was 12 minutes, as opposed to 2 minutes. The 12-minute passivation period resulted in the formation of a bright purple passivation film.

Example 4

The solution and process described in Example 1 was repeated, however, on this occasion the time period over which passivation was carried out was 18 minutes, as opposed to 2 minutes. The 18-minute passivation period resulted in the formation of a bright green passivation film.

Example 5

The solution and process described in Example 1 was employed. Again the solution was maintained at 20°C and commercial grade zinc anodes were used. Prior to plating, a standard commercially available saturated calomel reference electrode was immersed into the solution, and connected to the negative terminal of a voltmeter.

A mild steel article was immersed in the solution and electroplating carried out at 1A/dm2 for 20 minutes. The positive terminal of the voltmeter was connected to

the steel cathode, and a reading of -1.30V was obtained during electroplating. The current was turned off after 20 minutes, and the open circuit voltage of the fresh zinc coating was -1.01V. Immediately, current was again applied such that the voltage was held at -1.11V. This represented the application of a cathodic overvoltage to the zinc coating of 0.1V. The cathodic overvoltage was applied for 5 minutes, during which time, the passivation film was observed to form. A bright pink coloured passivation film was obtained.

Example 6

The solution in Example 1 was employed, at 20°C and using commercial grade zinc anodes. A steel article was immersed in the solution and electroplating carried out at 2A/dm2 for 2 minutes, sufficient to form a zinc coating of 2μm thickness. The current was then turned off. The coated article was then in contact with the solution for a further 90 seconds, during which time a light yellow passivation film was formed. Instead of removing the passivated and coated article from the solution, electroplating was again carried out at $2A/dm^2$ for 2 minutes. The current was then turned off, and an electrodeposited coating had formed over the surface of the underlying light yellow passivation film. The coated article was then in contact with the solution for 90 seconds, during which time a light yellow passivation film was again formed. This procedure of electroplating at $2A/dm^2$ for 2 minutes, followed by passivation for 90 seconds was twice repeated. Electroplating at $2A/dm^2$ for 2 minutes was then again carried out, and the current turned off. A final passivation film was produced through

contact with the solution for 1.75 minutes, which yielded a bright violet passivation film.

The resulting multi-layer coating consisted of five 2μm thick zinc layers, with four passivation films alternating between the zinc layers, and an outer bright violet passivation film.

Example 7

A water solution comprised 100g/L zinc chloride, 1g/L sodium tungstate, 1g/L sodium metavanadate, 1g/L sodium periodate, 5g/l thiamine hydrochloride, and 5g/L sodium thiosulphate. The solution was maintained at 25°C. Commercial grade zinc anodes were used. A mild steel article was immersed in the solution and electroplating carried out at $1A/dm^2$ for 20 minutes, which was sufficient to provide a zinc deposit of approximately 10μm. The current was turned off, and the coated article permitted to remain immersed in the solution for a further 2 minutes, during which time a passivation film was observed to form on the coating surface. The resulting passivation film was pale blue in colour, with a bright reflective appearance.

Example 8

A water solution comprised 60g/L zinc chloride, $ZnCl_2$, 45g/L nickel chloride, $NiCl_2$, 100g/L ammonium chloride, NH_4Cl, 1g/L sodium molybdate, Na_2MoO_4, 1g/L ammonium peroxodisulphate $(NH_4)_2S_2O_8$, and 1g/L sodium lauryl sulphate surfactant.

The solution was maintained at 20°C. Commercial grade zinc anodes were used. A mild steel article was immersed in the solution and electroplating carried out at 1A/dm^2 for 20 minutes, which was sufficient to provide a zinc-10 weight percent nickel alloy deposit of approximately 10μm. The current was turned off, and the coated article permitted to remain immersed in the solution for a further 5 minutes, during which time a passivation film was observed to form on the coating surface.

The resulting passivation film was an intense purple colour, with a bright reflective appearance.

Example 9

A water solution comprised 60g/L zinc chloride, $ZnCl_2$, 20g/L cobalt chloride, $CoCl_2$, 100g/L ammonium chloride, NH_4Cl, 1g/L sodium molybdate, Na_2MoO_4, 1g/L ammonium peroxodisulphate $(NH_4)_2S_2O_8$, and 1g/L sodium lauryl sulphate surfactant.

The solution was maintained at 20°C. Commercial grade zinc anodes were used. A mild steel article was immersed in the solution and electroplating carried out at 1A/dm^2 for 20 minutes, which was sufficient to provide a zinc-0.6 weight percent cobalt alloy deposit of approximately 10μm thickness. The current was turned off, and the coated article permitted to remain immersed in the solution for a further 6 minutes, during which time a passivation film was observed to form on the coating surface.

The resulting passivation film was an intense yellow-orange colour, with a bright reflective appearance.

Example 10

A water solution comprised 8g/L zinc oxide, 90g/L sodium hydroxide, NaOH, 1g/L sodium molybdate, Na_2MoO_4, 1g/L sodium tungstate, $NaWO_4$, 1g/L ammonium peroxodisulphate $(NH_4)_2S_2O_8$, and 1mL/L 30 Vol hydrogen peroxide.

The solution was maintained at 25°C. Commercial grade zinc anodes were used. A mild steel article was immersed in the solution and electroplating carried out at $1A/dm^2$ for 10 minutes, which was sufficient to provide a zinc deposit of approximately 8μm. The current was turned off, and the coated article permitted to remain immersed in the solution for a further 15 minutes, during which time a bright blue passivation film was observed to form on the coating surface.

Example 11

A water solution comprised 188g/L copper sulphate, $CuSO_4.5H_2O$, 75g/L sulphuric acid, 1g/L sodium molybdate, Na_2MoO_4, 1g/L sodium vanadate, $NaVO_3$, and 2.5g/L sodium metabisulphite, $Na_2S_2O_6^{2,}$ and 1g/L ammonium peroxodisulphate, $(NH_4)_2S_2O_8$.

The solution was maintained at 40°C. Commercial grade bagged copper anodes were used. A mild steel article was immersed in the solution and electroplating carried out at $5A/dm^2$ for 2 minutes, which was sufficient

to provide a copper deposit of approximately 10μm. The current was turned off, and the coated article permitted to remain immersed in the solution for a further 15 minutes, during which time a bright red passivation film was observed to form on the coating surface.

Example 12

A water solution comprised 72g/L stannous sulphate, 50g/L sulphuric acid, 40g/L phenolsulphonic acid, 2g/L gelatin, 1g/L beta-napthol, 1g/L sodium molybdate, Na_2MoO_4, and 1g/L ammonium peroxodisulphate, $(NH_4)_2S_2O_8$.

The solution was maintained at 23°C. Commercial grade tin anodes were used. A mild steel article was immersed in the solution and electroplating carried out at $1A/dm^2$ for 10 minutes, which was sufficient to provide a tin deposit of approximately 5μm. The current was turned off, and the coated article permitted to remain immersed in the solution for a further 8 minutes, during which time a bright yellow passivation film was observed to form on the coating surface.

Example 13

A water solution comprised 100g/L-manganese sulphate, 75g/L, 60g/l ammonium thiocyanate, 1g/L sodium molybdate, Na_2MoO_4, and 1g/L ammonium peroxodisulphate, $(NH_4)_2S_2O_8$.

The solution was maintained at 25°C. Commercial grade stainless steel anodes were used. A mild steel article was immersed in the solution and electroplating carried out at $2A/dm^2$ for 20 minutes, which was sufficient

to provide a manganese deposit of approximately 10μm. The current was turned off, and the coated article permitted to remain immersed in the solution for a further 8 minutes, during which time a bright red-green passivation film was observed to form on the coating surface.

Example 14

A water solution comprised 60g/L zinc chloride, $ZnCl_2$, 100g/L ammonium chloride, NH_4Cl, 1g/L sodium molybdate, Na_2MoO_4, 1g/L ammonium peroxodisulphate $(NH_4)_2S_2O_8$, and 1g/L sodium lauryl sulphate surfactant.

The solution was maintained at 20°C. Commercial grade zinc anodes were used. A mild steel article was immersed in the solution and electroplating carried out at $1A/dm^2$ for 20 minutes, which was sufficient to provide a zinc deposit of approximately 10μm. The current was turned off, and the coated article removed from the solution.

The un-passivated zinc coating was bright and reflective, with a slight blue tint when angled in light.

Example 15

A water solution comprised 60g/L zinc chloride, 150g/L ammonium chloride, 1.0g/L sodium molybdate, and 1.0g/L sodium lauryl sulphate surfactant.

The solution was maintained at 20°C. Commercial grade zinc anodes were used. A mild steel article was

immersed in the solution and electroplating carried out at 1A/dm^2 for 20 minutes. The current was then turned off, and the coated article permitted to remain immersed in the static solution for a further 3 minutes, after which it was removed, rinsed, and dried.

The result was a zinc coating furnished with a dark blue passivation film.

Example 16

A water solution comprised 60g/L zinc chloride, 150g/L ammonium chloride, 1.0g/L sodium tungstate, and 1.0g/L sodium lauryl sulphate surfactant.

The solution was maintained at 20°C. Commercial grade zinc anodes were used. A mild steel article was immersed in the solution and electroplating carried out at 1A/dm^2 for 20 minutes. The current was then turned off, and the coated article permitted to remain immersed in the static solution for a further 8 minutes, after which it was removed, rinsed, and dried.

The result was a zinc coating furnished with a light golden colour passivation film.

Example 17

A water solution comprised 60g/L zinc chloride, $ZnCl_2$, 150g/L ammonium chloride, NH_4Cl, 1.0g/L sodium molybdate, 1.0g/L ammonium peroxodisulphate, 1g/L sodium lauryl sulphate, and 1g/L sodium metabisulphite.

The solution was maintained at 20°C. Commercial grade zinc anodes were used. A mild steel article was immersed in the solution and electroplating carried out. The current density initially applied was 0.5A/dm^2 for 5 minutes under static conditions. The current density was then immediately increased to 1.0A/dm^2. After 5 minutes of plating at this current density under static conditions, circulation pumps were activated. After a period of 10 minutes of further plating at 1.0A/dm^2, the pumps were turned off and static conditions restored. A final plating period of 2 minutes at 1.0A/dm^2 followed. The current was then turned off, and the coated article permitted to remain immersed in the static solution for a further 8 minutes, during which time the passivation film was observed to form on the coating surface.

The resulting coating comprised a 12-micron thick zinc coating furnished with a bright yellow passivation film.

Example 18

A water solution comprised 60g/L zinc chloride, $ZnCl_2$, 150g/L ammonium chloride, NH_4Cl, 1.0g/L sodium molybdate, 1.0g/L ammonium peroxodisulphate, 1g/L sodium lauryl sulphate, and 1g/L sodium metabisulphite.

The solution was maintained at 20°C. Commercial grade zinc anodes were used. A mild steel article was immersed in the solution and electroplating carried out. The current density initially applied was 0.5A/dm^2 for 5 minutes under static conditions. The current density was then immediately increased to 1.0A/dm^2. After 5 minutes of plating at this current density under static conditions,

circulation pumps were activated such that gentle turbulence was produced around the article, and which was not unidirectional. After a period of 10minutes of further plating at 1.0A/dm^2, the pumps were turned off and static conditions restored. A final plating period of 2 minutes at 1.0A/dm^2 followed. The current was then turned off, and the coated article permitted to remain immersed in the solution. The circulation pumps were then reactivated for a period of 3 minutes, during which time a passivation film was observed to form on the coating surface.

The resulting coating comprised a 12-micron thick zinc coating furnished with a bright yellow-purple passivation film with an attractive mottled appearance.

Example 19

A water solution comprised 60g/L zinc chloride, $ZnCl_2$, 150g/L ammonium chloride, NH_4Cl, 1.0g/L sodium molybdate, 1.0g/L ammonium peroxodisulphate, 1g/L sodium lauryl sulphate, and 1g/L sodium metabisulphite.

The solution was maintained at 20°C. Commercial grade zinc anodes were used. A mild steel article was immersed in the solution and electroplating carried out at 1.0 A/dm^2 for a period of 10 minutes. At two-minute intervals, the bus bar holding the steel article was moved by approximately 5 cm from its original position, in a sideways movement. This action assisted in the removal of any hydrogen bubbles from the surface and any streaking effects they may otherwise have caused. The current was then turned off, and the coated article permitted to remain immersed in the static solution for a

further 8 minutes, during which time a passivation film was observed to form on the coating surface.

The resulting coating comprised a 12 micron thick zinc coating furnish with a bright yellow passivation film, where the colour was uniform over the entire sample surface.

Example 20

A water solution comprised 60g/L zinc chloride, $ZnCl_2$, 150g/L ammonium chloride, NH_4Cl, 0.8g/L sodium molybdate, 0.8g/L ascorbic acid, and 1g/L sodium lauryl sulphate surfactant.

The solution was maintained at 20°C. Commercial grade zinc anodes were used. A mild steel article was immersed in the solution and electroplating carried out at 1A/dm2 for 20 minutes. To promote the formation of the electrodeposited zinc coating, during the initial 10 minutes of electroplating, the solution was maintained in a static condition. Circulation pumps were then activated as described in Example 16, and plating continued under conditions of solution agitation. After 8 minutes under these conditions, the pumps were turned off, and plating continued for a further 2 minutes under static conditions. The current was then turned off, and the coated article permitted to remain immersed in the static solution for a further 8 minutes, during which time a passivation film was observed to form on the coating surface.

The resulting coating comprised a 10 micron thick zinc coating furnish with a bright purple-green passivation film.

Example 21

A water solution comprised 60g/L zinc chloride, $ZnCl_2$, 150g/L ammonium chloride, NH_4Cl, 1.0g/L sodium molybdate, 1.0g/L salicylic acid, and 1g/L sodium lauryl sulphate surfactant.

The solution was maintained at 20°C. Commercial grade zinc anodes were used. A mild steel article was immersed in the solution and electroplating carried out at 1A/dm2 for 20 minutes. To promote the formation of the electrodeposited zinc coating, during the initial 10 minutes of electroplating, the solution was maintained in a static condition. Circulation pumps were then activated as described in Example 16, and plating continued under conditions of solution agitation. After 8 minutes under these conditions, the pumps were turned off, and plating continued for a further 2 minutes under static conditions. The current was then turned off, and the coated article permitted to remain immersed in the static solution for a further 8 minutes, during which time a passivation film was observed to form on the coating surface.

The resulting coating comprised a 10 micron thick zinc coating furnish with a bright purple-green passivation film.

Example 22

A water solution comprised 60g/L zinc chloride, 15g/L nickel chloride, 100g/L potassium chloride, 0.8g/L sodium molybdate, 0.8g/L ascorbic acid, and 1g/L sodium lauryl sulphate surfactant.

The solution was maintained at 40°C. Commercial grade zinc anodes were used. A mild steel article was immersed in the solution and electroplating carried out at 1A/dm2 for 20 minutes. To promote the formation of the electrodeposited zinc-rich alloy coating, during the initial 10 minutes of electroplating, the solution was maintained in a static condition. During the following 8 minutes of electroplating, the solution was agitated through the use of circulation pumps. The final two-minute period of plating was carried out with the pumps turned off. The current was then turned off, and the coated article permitted to remain immersed in the solution for a further 8 minutes, during which time the passivation film was observed to form on the coating surface.

The resulting coating comprised a 10-micron thick zinc-10 weight per cent nickel alloy coating furnish with a bright yellow-purple passivation film.

Example 23

The solution in Example 20 was employed, at 20°C and using stainless steel anodes. A steel article was immersed in the static solution and electroplating carried out under static conditions at 1A/dm^2 for 60 seconds, sufficient to form a 0.5μm zinc coating. The current was then turned off. The coated article was then in contact with the solution for a further 60 seconds,

during which time a light blue passivation film was formed. Instead of removing the passivated and coated article from the solution, electroplating was again carried out at 1A/dm^2 for 60 seconds. The current was then turned off, and an electrodeposited coating had formed over the surface of the underlying passivation film. This procedure of electroplating at 1A/dm^2 for 60 seconds, followed by passivation for 60 seconds was repeated seven times. Electroplating at 1A/dm^2 for 5 minutes was then carried out with circulation pumps activated. The current and the pumps were then turned off. A final passivation film was produced through contact with the solution for 8 minutes under static conditions, which yielded a bright yellow passivation film.

The resulting coating comprised multiple 0.5µm thick zinc layers, with passivation films sandwiched between the zinc layers, and an outer bright yellow passivation film.

Example 24

A water solution comprised 60g/L zinc chloride, $ZnCl_2$, 100g/L ammonium chloride, NH_4Cl, 0.2g/L sodium molybdate, 0.8g/L sodium tungstate, 1g/L sodium lauryl sulphate surfactant, 1g/L sodium metabisulphite, and 0.1g/L thiamine hydrochloride.

The solution was maintained at 20°C. Commercial grade zinc anodes were used. A mild steel article was immersed in the solution and electroplating carried out at 1A/dm2 for 20 minutes, during which time circulation pumps were operated continuously. The current was turned off, and the coated article permitted to remain immersed

in the agitated solution for a further 2 minutes, during which time a passivation film was observed to form on the coating surface.

The result was a zinc deposit of approximately 10μm furnished with a lilac coloured passivation film.

Example 25

A water solution comprised 60g/L zinc chloride, $ZnCl_2$, 100g/L ammonium chloride, NH_4Cl, 0.2g/L sodium molybdate, 0.8g/L sodium tungstate, 1g/L sodium lauryl sulphate surfactant, 1g/L sodium metabisulphite, and 0.1g/L thiamine hydrochloride.

The solution was maintained at 20°C. Commercial grade zinc anodes were used. A mild steel article was immersed in the solution and electroplating carried out at 1A/dm2 for 20 minutes, during which time circulation pumps were operated continuously. The current was turned off, and the coated article permitted to remain immersed in the agitated solution for a further 6 minutes, during which time a passivation film was observed to form on the coating surface.

The result was a zinc deposit of approximately 10μm thickness furnished with a bright purple-green passivation film.

Example 26

A water solution comprised 60g/L zinc chloride, 15g/L cobalt chloride, 150g/L ammonium chloride, 0.2g/L

sodium molybdate, 0.8g/L sodium tungstate, and 1g/L sodium lauryl sulphate surfactant.

The solution was maintained at 30°C. Commercial grade zinc anodes were used. A mild steel article was immersed in the solution and electroplating carried out at 1A/dm2 for 20 minutes, during which time circulation pumps were operated continuously. The current was turned off, and the coated article permitted to remain immersed in the agitated solution for a further 2 minutes, during which time a passivation film was observed to form on the coating surface.

The result was a zinc-0.6 weight per cent cobalt alloy deposit of approximately 10μm thickness furnished with a bright blue-yellow passivation film.

Example 27

A water solution comprised 60g/L zinc chloride, $ZnCl_2$, 150g/L ammonium chloride, NH_4Cl, 0.2g/L sodium molybdate, 0.8g/L sodium tungstate, 1g/L sodium lauryl sulphate surfactant, 1g/L sodium metabisulphite, and 0.1g/L thiamine hydrochloride.

The solution was employed at 20°C and using commercial zinc anodes. A steel article was immersed in the solution, with circulation pumps activated, and electroplating carried out under static conditions at $1A/dm^2$ for 60 seconds, sufficient to form a 0.5μm zinc coating. The current was then turned off. The coated article was then in contact with the solution for a further 60 seconds, during which time a dark yellow passivation film was formed. Instead of removing the

passivated and coated article from the solution, electroplating was again carried out at 1A/dm^2 for 60 seconds. The current was then turned off, and an electrodeposited coating had formed over the surface of the underlying passivation film. This procedure of electroplating at 1A/dm^2 for 60 seconds, followed by passivation for 60 seconds was repeated seven times, in all cases with the circulation pumps activated. Electroplating at 1A/dm^2 for 5 minutes was then carried out with circulation pumps activated. The current was then turned off. A final passivation film was produced through contact with the agitated solution for 5 minutes, which yielded a bright purple-green passivation film.

The resulting coating comprised multiple 0.5μm thick zinc layers, with passivation films sandwiched between the zinc layers, and an outer bright purple-green passivation film.

Example 28

A water solution comprised 60g/L zinc chloride, 110g/L potassium chloride, 0.2g/L sodium molybdate, 0.8g/L sodium tungstate, 0.2g/L ascorbic acid, 0.15g/L ammonium peroxodisulphate, and 1g/L sodium lauryl sulphate surfactant.

The solution was maintained at 20°C. Commercial grade zinc anodes were used. A mild steel article was immersed in the solution and electroplating carried out at 1A/dm^2 for 20 minutes, during which time circulation pumps were operated continuously. The current was turned off, and the coated article permitted to remain immersed in the agitated solution for a further 2 minutes, during

which time a passivation film was observed to form on the coating surface.

The result was a zinc deposit of approximately 10μm thickness furnished with a bright iridescent passivation film.

Example 29

A water solution comprised 188g/L copper sulphate ($CuSO_4$. $5H_2O$), 75g/L sulphuric acid, 0.4g/L sodium molybdate, 1.2g/l sodium tungstate, 2.5g/L sodium metabisulphite, and 0.2g/L sodium lauryl sulphate.

The solution was maintained at 40°C. Commercial grade bagged copper anodes were used. A mild steel article was immersed in the static solution and electroplating carried out at 5A/dm2 for 2 minutes, which was sufficient to provide a copper deposit of approximately 10μm thickness. The current was turned off, and the coated article permitted to remain immersed in the solution for a further 5.5 minutes, during which time a yellow passivation film was observed to form on the coating surface.

Example 30

A water solution comprised 72g/Lstannous sulphate, 50g/L sulphuric acid, 40g/L phenolsulphonic acid, 2g/L gelatin, 1g/L beta-napthol, 0.5g/L sodium molybdate, and 0.6g/L sodium tungstate.

The solution was maintained at 25°C. Commercial grade tin anodes were used. A mild steel article was

immersed in the solution and electroplating carried out at 1A/dm2 for 10 minutes under static conditions. This was sufficient to provide a tin deposit of approximately 6μm. The current was turned off, and the coated article permitted to remain immersed in the solution for a further 4 minutes, during which time a bright yellow passivation film was observed to form on the coating surface.

Example 31

A water solution comprised 100g/L manganese sulphate, 75g/L ammonium thiocyanate, 0.4g/L sodium molybdate, and 1.2g/L sodium tungstate.

The solution was maintained at 25°C. Commercial grade stainless steel anodes were used. A mild steel article was immersed in the solution and electroplating carried out at 2A/dm^2 for 20 minutes, which was sufficient to provide a manganese deposit of approximately 10μm. The current was turned off, and the coated article permitted to remain immersed in the solution for a further 5 minutes, during which time a bright red-green passivation film was observed to form on the coating surface.

Example 32

A water solution comprised 300g/L nickel sulphate, 40g/L nickel chloride, 35g/L boric acid, 0.1g/L sodium lauryl sulphate, 0.2g/L sodium molybdate, and 0.8g/L sodium tungstate.

The solution was maintained at 55°C. Commercial grade nickel anodes were used. A mild steel article was

immersed in the static solution and electroplating carried out at 5A/dm^2 for 10 minutes. The current was turned off, and the coated article permitted to remain immersed in the solution for a further 4 minutes, again under static conditions, during which time an iridescent yellow passivation film was observed to form on the coating surface.

Example 33

A water solution comprised 60g/L zinc chloride, $ZnCl_2$, 100g/L ammonium chloride, NH_4Cl, 0.2g/L sodium molybdate, 0.8g/L sodium tungstate, 1g/L sodium lauryl sulphate surfactant, 1g/L sodium metabisulphite, and 0.1g/L thiamine hydrochloride.

The solution was maintained at 25°C. Commercial grade zinc anodes were used. A mild steel article was immersed in the solution with circulation pumps activated. A current density of 2 A/dm^2 was applied for 15 minutes. The current was then turned off and the sample removed, followed by rinsing and drying.

The result was a zinc coating of approximately 10 microns thickness.

Several tests were performed on zinc type coatings prepared according to the earlier examples. These were a zinc coating without a passivation film, and zinc coatings with blue, yellow, and purple films, all produced according to the present invention. Multi-layer coatings prepared according to the present invention were also assessed. Commercially deposited zinc coatings, with and without yellow chromate passivation films, were

included in the tests for comparison purposes. All of the coatings were of 10μm thickness.

The first test conducted was to allow comparison of corrosion resistance. The samples were placed in separate baths of aerated 5 percent sodium chloride solution. The time to failure was determined as the time to the formation of red rust corrosion products, namely the point where the coating had failed and permitted the corrosion of the underlying steel.

The second test was conducted on a separate batch of samples, and involved applying adhesive tape to the surface. If on pulling back the tape, none of the underlying coating or film was visible on the tape, then this indicated adequate adhesion. Any signs of the coating or film on the tape indicated adhesion failure.

The third test again required a separate batch. On this occasion, epoxy paint was applied to the coating or film surface. When dried, the paint was crosshatched several times with a sharp knife. The adhesion tape tests were then applied as above. If on pulling back the tape, none of the paint was visible on the tape, then this indicated adequate adhesion of the paint to the underlying coating or film. Any signs of the paint on the tape indicated adhesion failure.

Several tests were performed on zinc type coatings prepared using solutions comprising molybdate and tungstate alone, molybdate and ascorbic acid, and molybdate - tungstate combinations.

Table 1 provides a summary of the test data obtained.

Table 1

Zinc Coating	Passivation film	Time to red rust (Hours)	Film adhesion test	Paint adhesion test
Commercial	None	48	Not applicable	Fail
Commercial	Chromated	720	Pass	Pass
As example 14	None	144	Not applicable	Pass
As example 1	Blue Film	672	Pass	Pass
As example 2	Yellow Film	840	Pass	Pass
As example 3	Purple Film	1080	Pass	Pass
As example 6	Multi-layer	1920	Pass	Pass
As example 15	Blue Film	96	Pass	Pass
As example 16	Golden Film	72	Pass	Fail
As example 20	Purple-Green	960	Pass	Pass
As example 33	None	168	Not Applicable	Pass
As example 24	Lilac	720	Pass	Pass
As example 25	Purple-Green	960	Pass	Pass

As example 27	Multilayer	2000+	Pass	Pass

The table shows that commercial un-passivated zinc coatings developed red rust, i.e. the corrosion products of the underlying steel substrate, in 48 hours. In contrast, un-passivated zinc coatings from the solution of Example 14 prevented red rust for 144 hours i.e. a three-fold improvement over commercial zinc. These findings confirm that zinc coatings produced from solutions of the present invention are more corrosion resistant than those produced from conventional electroplating solutions. It is considered that a small concentration of the film forming species are integrated within the zinc coating during electrodeposition. These film forming species are further considered to leach from the zinc coating during contact with a corrodent, and act to inhibit corrosion, thereby accounting for the improved levels of corrosion resistance.

Commercial chromated zinc delayed the onset of red rust for 720 hours, showing the effectiveness of chromate passivation films in reducing corrosion. The zinc coating with a blue passivation from Example 1 was marginally less effective than chromated zinc, however, the zinc coatings with yellow (Example 2) and purple (Example 3) passivation films provided greater corrosion resistance than chromate. This demonstrates that the coatings and films of the current invention exceed the overall levels of corrosion protection afforded by chromate.

Example 6 refers to a multi-layer coating. This coating comprises five 2μm thick zinc layers, with four

passivation films alternating between the zinc layers, and an outer bright violet passivation film. This multi-layer coating exhibited corrosion resistance approaching three times that of chromated zinc of the same overall thickness. During corrosive attack, the penetration of the outer passivation film and the outer zinc layer, does not lead to coating breakdown, as is the case with conventional coatings consisting of a single zinc layer with a single passivation film. Instead, the corrodent comes into contact with a further protective passivation film. Indeed the corrodent must penetrate through ten separate layers of either zinc or passivation film before the steel is exposed, as opposed to just two layers with a conventional coating system. The ten separate layers thus act as a brake on the progress of corrosion through the coating, thus accounting for the superior corrosion resistance observed.

The table shows that the range of passivation films produced according to the present invention exhibited satisfactory adhesion of the film to the underlying coating. As anticipated, commercial un-passivated zinc failed the paint adhesion test, since the relatively loose air-formed oxide film on the zinc presents an unsatisfactory surface for bonding with paint. In contrast, Example 14, the un-passivated zinc coating produced according to the present invention, demonstrated excellent paint adhesion. This is considered to arise from the greatly reduced tendency of zinc coatings of the current invention to oxidise in the atmosphere. Paint adhesion to chromate and the passivated coatings of the current invention (Examples 1, 2, 3 and 6) was found to be excellent with no signs of adhesion loss.

The coatings and films that were produced from solutions containing molybdate alone (Example 15) afforded an improvement in corrosion resistance over commercial zinc. The film adhesion to the underlying coating, and paint adhesion were both found to be acceptable. The corrosion resistance found with tungstate (Example 16) was of a similar order to that found with molybdate (Example 15), however, the main difference was that paint adhesion to the 'tungstate films' was found to be comparatively less.

Example 20 was produced in the presence of solutions containing molybdate and ascorbic acid. The corrosion resistance of the coatings and films was slightly lower than found with those films of similar colour produced in the presence of molybdate and peroxide salt (e.g. Example 3), however, film adhesion and paint adhesion were satisfactory.

Example 33 was produced from solutions containing molybdate and tungstate, however, no film was permitted to form. The resistance to red rust formation seen with this example exceeded that of Example 14, namely a zinc coating of similar thickness produced from a solution containing molybdate and peroxide salt. This suggests that the combination of molybdate and tungstate has a particularly beneficial effect on corrosion resistance.

With Examples 24 and 25, the coatings were produced with passivation films from solutions containing molybdate and tungstate. In all of the tests, these samples performed in a similar manner to those produced from molybdate - peroxo salt containing solutions. Example 27 related to a multi-layer comprising thin

layers of zinc with a passivation film between each layer, and an outer bright yellow passivation film. The most interesting test result for this sample was in terms of corrosion resistance. The corrosion test was halted after 2000 hours, since no red rust had been observed after this substantial time period, which was around three times longer than that seen for the chromated zinc control sample. It is thought that the presence of the corrosion resistant passivation films within the zinc coating is largely responsible for the major improvements seen in the corrosion test, particularly when compared with the more usual dual layer coatings.

Claims

1. An electrolyte solution comprising at least one plateable metal ion capable of being reduced to the metallic form, at least one transition metal ion species, and a solvent, in which a passivated coating of the at least one plateable metal ion can be deposited on an article.

2. An electrolyte solution according to Claim 1, in which the at least one plateable metal ion is selected from: Ag^{+}, Au^{+}, Au^{3+}, Bi^{3+} Cd^{2+}, Co^{2+}, Cr^{3+}, Cr^{6+}, Cu^{+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, In^{+}, In^{3+}, Mn^{2+}, Mn^{3+}, Mn^{4+}, Ni^{2+}, Pb^{2+}, Pb^{4+}, Pd^{2+}, Pt^{2+}, Rh^{2+}, Rh^{3+}, Sn^{2+}, Sn^{3+}, Sn^{4+}, Sb^{3+}, Sb^{4+}, Sb^{5+}, Zn^{2+}.

3. An electrolyte solution according to any preceding Claim, in which the at least one plateable metal ion is selected from: Ag^{+}, Co^{2+}, Cu^{+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Mn^{3+}, Mn^{4+}, Ni^{2+}, Sn^{2+}, Zn^{2+}.

4. An electrolyte solution according to any preceding Claim, in which a counter ion to the at least one plateable metal ion may comprise any ion that gives rise to a salt of sufficient solubility in the chosen solvent.

5. An electrolyte solution according to Claim 4, in which concentration of salt or salts comprising the at least one plateable metal will preferably be in a range of 0.1 to 500g/L.

6. An electrolyte solution according to any preceding Claim, in which the at least one transition metal ion species is formed from reaction in solution between at least one transition metal ion species and at least one film forming agent.

7. An electrolyte solution according to any preceding Claim, in which the at least one transition metal ion species is a suitable species of at least one metal from the transition metal block of the periodic table.

8. An electrolyte solution according to any preceding Claim, in which the at least one transition metal ion species is chosen from: Ti^{2+}, Ti^{3+}, Ti^{4+}, V^{5+}, V^{4+}, V^{3+}, V^{2+}, Zr^{2+}, Zr^{3+}, Zr^{4+}, Nb^{5+}, Nb^{4+}, Nb^{3+}, Nb^{2+}, Mo^{6+}, Mo^{5+}, Mo^{4+}, Mo^{3+}, Mo^{2+}, Hf^{2+}, Hf^{3+}, Hf^{4+}, Ta^{5+}, Ta^{4+}, Ta^{3+}, Ta^{2+}, Re^{7+}, W^{6+}, W^{5+}, W^{4+}, W^{3+}, W^{2+}, Mn^{6+}.

9. An electrolyte solution according to any preceding Claim, in which the at least one transition metal ion species is an oxide or halide moiety of the at least one transition metal ion species, chosen from: TiO_3^{2-}, $Ti_3Cl_{12}^{3-}$, TiO_5^{6-}, $Ti_2O_7^{6-}$, $Ti_6O_{13}^{2-}$, TiF_6^{2-}, $Ti_3O_7^{2-}$, $Ti_5O_{16}^{12-}$, ZrO_3^{2-}, $Zr_3O_{12}^{12-}$, ZrO^{2-}, ZrF_6^{2-}, ZrO_9^{2-}, HfO^{2-}, HfF_6^{2-}, VO_3^-, VO_4^{3-}, $Nb_2O_6^{2-}$, $Nb_5O_{15}^{5-}$, NbF_7^{2-}, NbO_3^-, TaF_7^{2-}, TaO_3^-, $Ta_2O_6^{2-}$, MoO_4^{2-}, $Mo_3O_{12}^{6-}$, WO_4^{2-}, $W_4O_{16}^{8-}$, $W_3O_{12}^{6-}$, MnO_4^-, ReO_4^-.

10. An electrolyte solution according to any preceding Claim, in which the at least one transition metal ion species is an oxide moiety of the at least one transition metal ion species, chosen from: VO_3^-, VO_4^{3-}, MoO_4^{2-}, WO_4^{2-}, MnO_4^-.

11. An electrolyte solution according to any preceding Claim, in which MoO_4^{2-} and WO_4^{2-} are employed in the same solution.

12. An electrolyte solution according to any preceding Claim, in which the MoO_4^{2-} concentration is in the range 0.2 to 0.4g/L and the WO_4^{2-} concentration is in the range 0.8 to 1.2g/L.

13. An electrolyte solution according to any preceding Claim, in which the MoO_4^{2-} concentration is 0.2g/L and the WO_4^{2-} concentration is 0.8g/L.

14. An electrolyte solution according to any preceding Claim, in which the counter ion to the at least one transition metal ion species may comprise any cation that gives rise to a sufficiently soluble salt.

15. An electrolyte solution according to any preceding Claim, in which the concentration range of the salt or salts comprising the at least one transition metal ion species is 0.01 to 100g/L.

16. An electrolyte solution according to any preceding Claim, in which the at least one film forming agent is a species that is capable of reacting with the at least one transition metal ion species to form a complex of the at least one transition metal ion species such that the complex is furnished with film forming properties.

17. An electrolyte solution according to any preceding Claim, in which the at least one film forming agent is chosen from: ClO_4^-, $Cl_2O_2^{2-}$, NO_2^-, NO_3^-, PO_4^{3-}, SO_3^{2-}, $S_4O_6^{2-}$,

IO_3^-, IO_4^-, $O2^{2-}$, $(OOH)^-$, $(H2OOH)^+$, $P_2O_8^{4-}$, $S_2O_6^{2-}$, $S_2O_8^{2-}$, $C_2O_4^{2-}$, ascorbic acid, tartaric acid or salicyclic acid.

18. An electrolyte solution according to any preceding Claim, in which the at least one film forming agent is chosen from: $S_2O_8^{2-}$ O_2^{2-}, IO_3^-.

19. An electrolyte solution according to any preceding Claim, in which a counter ion to the at least one film forming agent may comprise any cation that gives rise to a sufficiently soluble salt.

20. An electrolyte solution according to any preceding Claim, in which the concentration range of the salt or salts comprising the at least one transition metal ion species is 0.01 to 1000g/L.

21. An electrolyte solution according to any preceding Claim, in which the concentration range of the salt or salts comprising the at least one transition metal ion species is 0.8 to 10g/L. However, concentrations outside these ranges may also be suitable as required.

22. An electrolyte solution according to any preceding Claim, in which the solvent is acidic, neutral, or alkaline

23. An electrolyte solution according to any preceding Claim, in which the solvent is water

24. An electrolyte solution according to any preceding Claim, in which the solution further comprises a surfactant.

25. An electrolyte solution according to any preceding Claim, in which the solution further comprises a conductivity salt.

26. An electrolyte solution according to any preceding Claim, in which the solution further comprises a buffer.

27. An electrolyte solution according to any preceding Claim, in which the solution further comprises a levelling agent.

28. An electrolyte solution according to any preceding Claim, in which the solution further comprises a brightening agent.

29. An electrolyte solution according to any preceding Claim, in which the solution further comprises a complexing agent.

30. A process for coating a substrate comprises contacting an article with a solution which comprises at least one plateable metal ion capable of being reduced to the metallic form, at least one transition metal ion species, and a solvent; and in which the article forms the cathode of an electrochemical cell, passing a current through the electrochemical cell such that the at least one plateable metal ion is electrodeposited on the article, lowering or turning off the current passing through the electrochemical cell such that the electrodeposition of the at least one plateable metal ion is substantially stopped, leaving the electrodeposited coating of the at least one plateable metal ion in contact with the solution such that the at least one

transition metal ion species forms a passivation film on the coating of the at least one plateable metal ion.

31. A process for coating a substrate comprises contacting an article with a solution which comprises at least one plateable metal ion capable of being reduced to the metallic form, at least one transition metal ion species, and a solvent; and in which the article forms the cathode of an electrochemical cell, comprising the steps of (a) passing a current through the electrochemical cell such that the at least one plateable metal ion is electrodeposited on the article, lowering or turning off the current passing through the electrochemical cell such that the electrodeposition of the at least one plateable metal ion is substantially stopped; followed by (b) leaving the electrodeposited coating of the at least one plateable metal ion in contact with the solution such that the at least one transition metal ion species forms a passivation film on the coating of the at least one plateable metal ion; wherein (a) and (b) are repeated any number of times, and in any order, to form a multi-layer coating comprising alternate layers of a coating of the at least one plateable metal ion and the passivation film formed from the at least one transition metal ion complex species.

32. A process for coating a substrate according to Claim 30 or Claim 31, in which is incorporated solution agitation.

33. A process for coating a substrate according to Claim 30 or Claim 31, in which is incorporated cathode movement.

34. A process for coating a substrate according to Claim 30 or Claim 31, in which is incorporated both solution agitation and cathode movement.

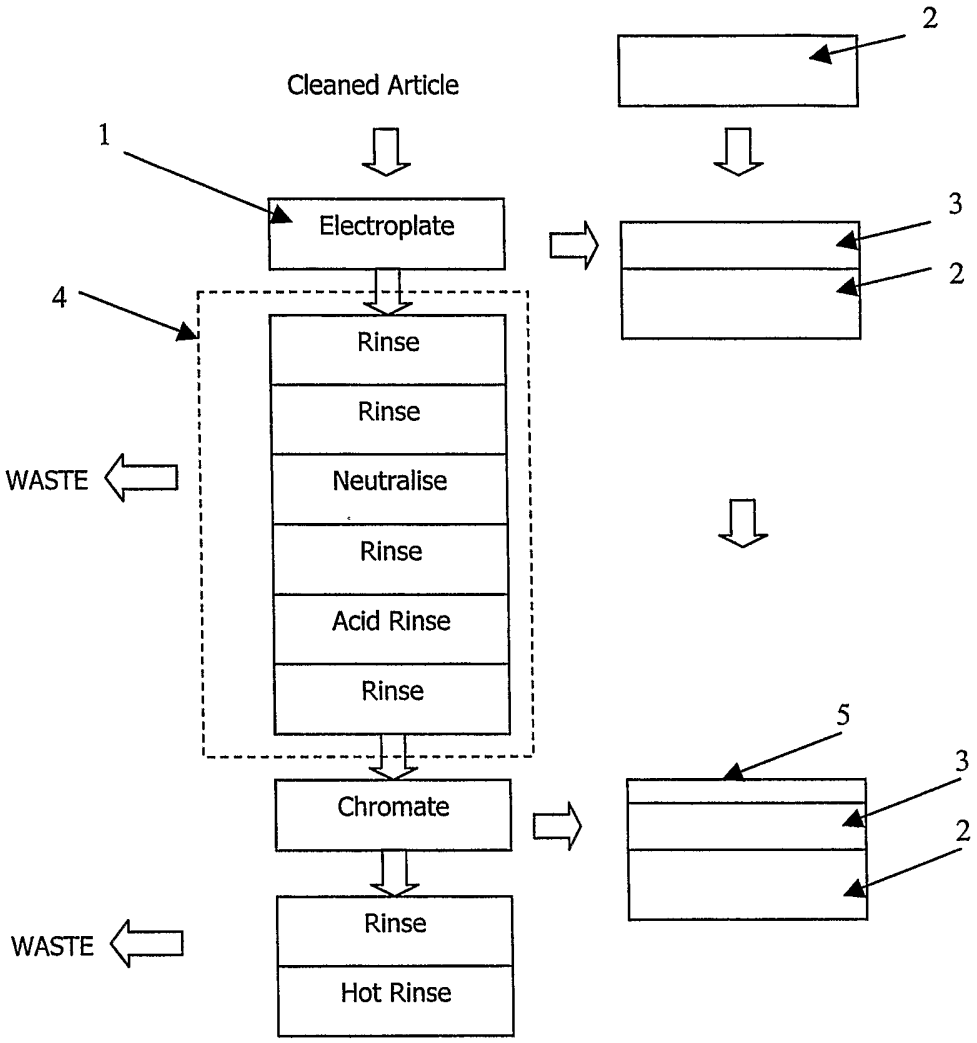
Cleaned Article
1
Electroplate
2
3
2
4
Rinse
Rinse
WASTE
Neutralise
Rinse
Acid Rinse
Rinse
5
3
2
Chromate
Rinse
WASTE
Hot Rinse

Figure 1

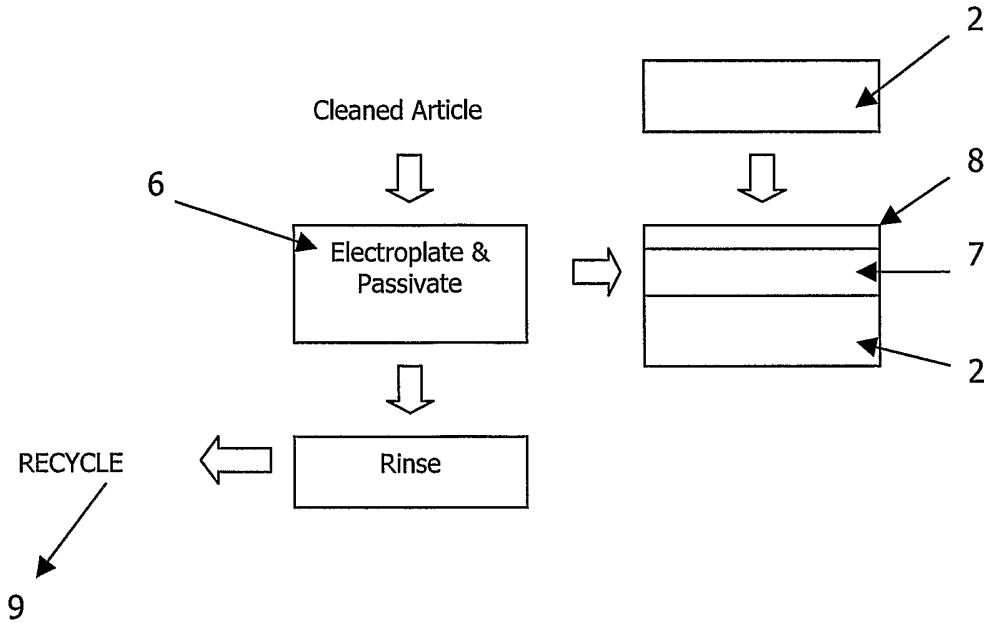
2
Cleaned Article
6
8
Electroplate &
Passivate
7
2
RECYCLE
Rinse
9

Figure 2

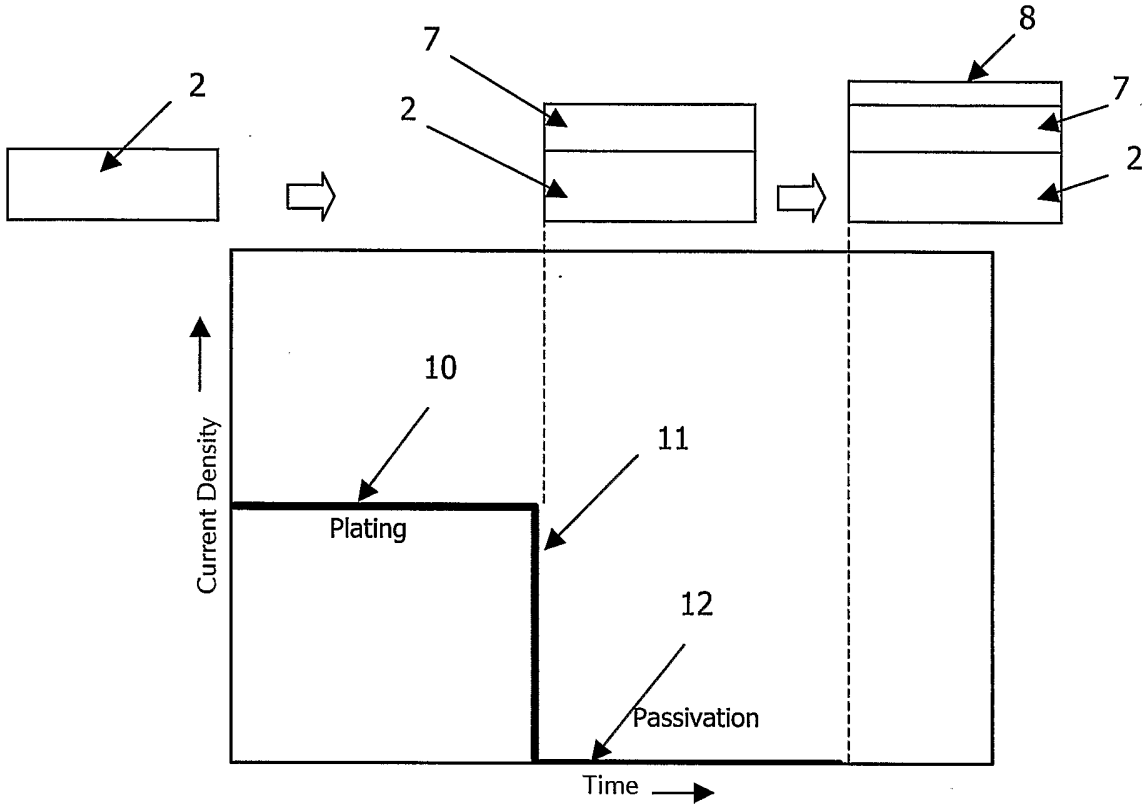

Figure 3

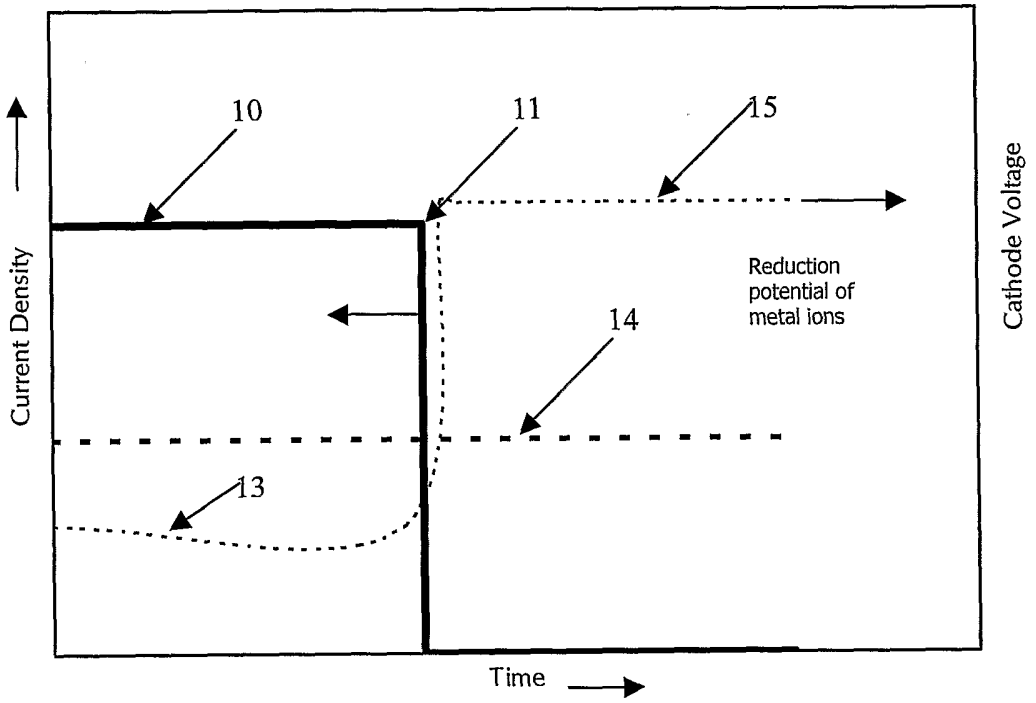
10
11
15
Current Density
Reduction
potential of
metal ions
Cathode Voltage
14
13
Time

Figure 4

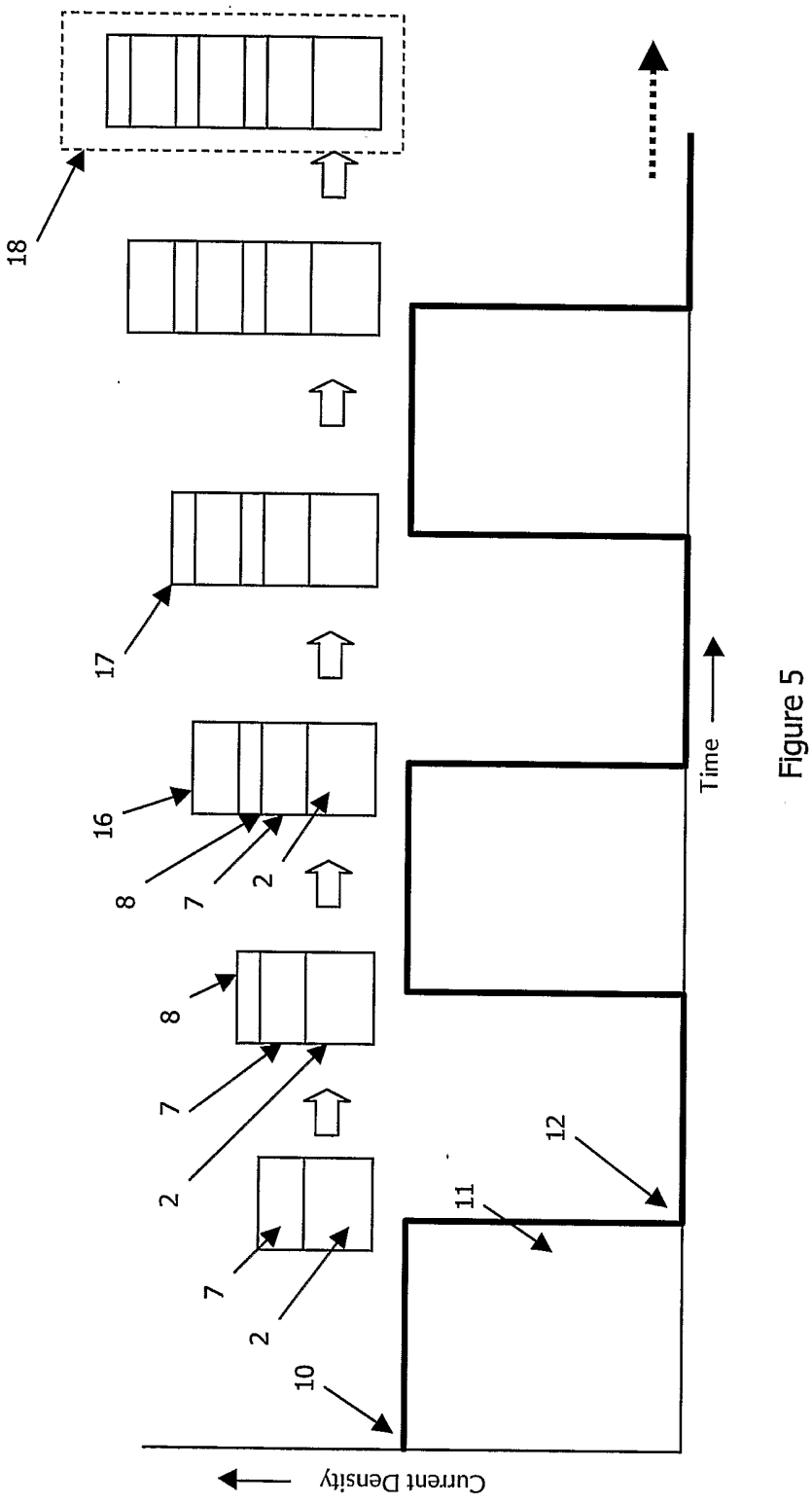

Figure 5

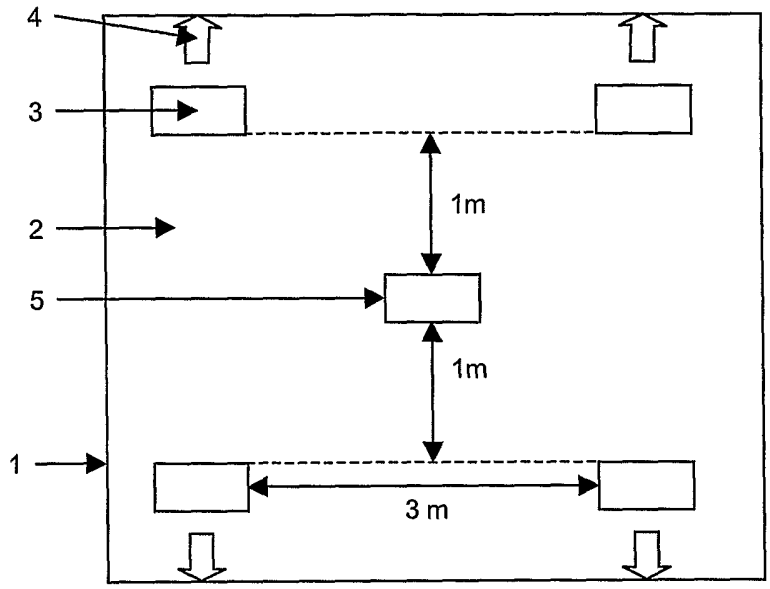

FIGURE 6

Box No. VIII (v) DECLARATION: NON-PREJUDICIAL DISCLOSURES OR EXCEPTIONS TO LACK OF NOVELTY

The declaration must conform to the standardized wording provided for in Section 215; see Notes to Boxes Nos. VIII, VIII (i) to (v) (in general) and the specific Notes to Box No. VIII (v). If this Box is not used, this sheet should not be included in the request.

Declaration as to non-prejudicial disclosures or exceptions to lack of novelty (Rules 4.17(v) and 51*bis*.1(a)(v)):

The inventions disclosed in the attached application were invented by Dr. Kevin Baldwin. Dr. Baldwin subsequently showed Mr. Ivan Ruzic of Bioharvest – Inter*Cat LLC/GmbH, and all related entities, around the premises where the inventions were being developed on 23rd January 2003. Dr. Baldwin and Bioharvest – Inter*Cat LLC/GmbH, and related entities, had a business relationship with regard to business development and investment. Before Mr. Ivan Ruzic was shown around the premises a confidentiality agreement confirming the confidential nature of the experiments concerning the inventions was agreed between the parties. During the tour Dr. Baldwin never handed over any written information with regard to the inventions themselves, nor did Mr. Baldwin actually tell Mr. Ivan Ruzic how they were prepared or properly executed, and no discussion of later experiments took place. However, Mr. Ivan Ruzic appreciated the possible value of these inventions and encouraged Dr. Baldwin to develop the inventions described in the attached application. Later the business relationship between Dr. Baldwin and Ivan Ruzic of Bioharvest – Inter*Cat LLC/GmbH, and all related entities, deteriorated and negotiations and discussions were stopped. The business relationship between Dr. Baldwin and Bioharvest – Inter*Cat LLC/GmbH, and related entities was terminated. Dr. Baldwin does not know if the information that Mr. Ivan Ruzic acquired during the business relationship has been subsequently disclosed contrary to the confidentiality agreement.

☐ This declaration is continued on the following sheet, "Continuation of Box No. VIII (v)".

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 03/03160

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C25D3/02 C25D5/48 C25D5/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C25D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 319 912 A (TOYO KOHAN CO LTD) 13 June 1973 (1973-06-13)	1-5, 7-11, 14-17, 20-23, 25,29,30
A	the whole document	12,13
X	DATABASE WPI Section Ch, Week 199238 Derwent Publications Ltd., London, GB; Class L03, AN 1992-314623 XP002273449 & SU 1 696 581 A (KHAMAEV V A) 7 December 1991 (1991-12-07) abstract	1-5, 7-11,14, 15, 20-23,30

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 March 2004	26/03/2004

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Van Leeuwen, R

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 03/03160

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 03, 29 March 1996 (1996-03-29) & JP 7 292491 A (HITACHI CABLE LTD), 7 November 1995 (1995-11-07) abstract	1-5, 7-11,14, 15, 20-23, 29,30

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 03/03160

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
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			AU	444789 B2	07-02-1974
			AU	3632971 A	07-06-1973
			BE	776651 A2	04-04-1972
			CA	955013 A1	24-09-1974
			DE	2141614 A1	06-07-1972
			FR	2117837 A1	28-07-1972
			NL	7117090 A ,B	19-06-1972
			ZA	7107936 A	30-08-1972
SU 1696581	A	07-12-1991	SU	1696581 A1	07-12-1991
JP 7292491	A	07-11-1995	NONE		