

Improvements in Coating Technology

The present invention concerns improvements in coating technology, more particularly it concerns improvements in the deposition of coatings of platinum by electroplating. Even more particularly, the present invention concerns improvements in the deposition of coatings of platinum by electroplating in a commercial or industrial process.

Electroplating is a well-known technique for applying coatings of platinum and other platinum group metals onto conductive substrates. Although most substrates for plating according to the present invention are conductive metals or graphite, composites incorporating conductive fibres or particles may be considered as well as plastics which have a keying metal deposit or flash coating. The coatings may be a thin "flash" coating used for jewellery, or several microns in thickness, generally up to about 20 μm , depending upon the intended use of the coated product; the coating may be thicker for certain applications. There are a number of major uses for functional (including protective as well as catalytic coatings) or decorative coatings, in jewellery, in electronics for depositing layers for memory applications or conductive tracks, and in the coating of turbine blades, where a platinum coating is used in the formation of protective aluminides. Two major types of ammoniacal platinum plating baths have been introduced by Johnson Matthey in the last few decades, namely "P Salt" and "Q salt[®]". "P salt" is an ammoniacal solution of diammine dinitroplatinum(II), i.e. $(\text{NH}_3)_2\text{Pt}(\text{NO}_2)_2$. "Q salt[®]" is an ammoniacal solution of tetraammineplatinum(II) hydrogen orthophosphate.

The teaching of EP0358375A is herein incorporated by reference in its entirety for all purposes. "Q Salt[®]" has been very successfully used in industry. Plating is carried out at temperatures of 90°C or above. At such temperatures, water vapour and ammonia are driven off, with the consequential need to regularly replenish these components during plating in order to maintain plating rate. Additionally, the platinum salt needs to be replenished with use of the bath. There have been attempts to find alternatives to ammonia but there remains a need to find plating baths which are more environmentally friendly in reducing or eliminating the loss of toxic ammonia, and desirably which are less energy intensive and/or which offer other advantages, such as having a good plating rate, good coating properties and compatible with plating additives that improve coating properties.

Most platinum plating is carried out under significantly alkaline conditions. For certain substrates, for which alkaline conditions encourage oxide or hydroxide formation or cause other difficulties, it would be desirable to operate under acidic or neutral to mildly alkaline conditions.

Summary of the invention

The present invention relates to a platinum plating bath. The bath may be used successfully over extended periods and the platinum component may be replenished easily. The bath has good thermal stability in general and as such generally requires simple maintenance and analytical control.

The bath may also be used over a wide range of pHs and, in certain preferred embodiments, provide

a safe, neutral non-corrosive bath. In certain embodiments, the baths yield a bright and shiny plate. In certain embodiments, the baths may be used under relatively energy-efficient conditions. In certain embodiments, the baths have a good plating rate providing a good deposition of platinum in a reasonable period of time. In certain embodiments and, depending on the platinum plating salt selected, the baths may be used without the emission of ammonia or with only low emissions.

In one aspect, the present invention provides an aqueous platinum electroplating bath comprising:

- a) a source of platinum ions; and
- b) a source of borate ions.

In another aspect, the invention provides the use of the aqueous platinum electroplating bath of the present invention for plating platinum onto a substrate.

Definitions

The point of attachment of a moiety or substituent is represented by "-". For example, -OH is attached through the oxygen atom.

"Alkyl" refers to a straight-chain or branched saturated hydrocarbon group. In certain embodiments, the alkyl group may have from 1 to 10 carbon atoms, in certain embodiments from 1 to 8 carbon atoms, in certain embodiments from 1 to 6 carbon atoms. The alkyl group may be substituted or unsubstituted. Unless otherwise specified, the alkyl group may be attached at any suitable carbon atom and, if substituted, may be substituted at any suitable carbon atom. Typical alkyl groups include but are not limited to methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl, n-hexyl, and the like.

"Alkenyl" refers to a straight-chain or branched unsaturated hydrocarbon group having at least one carbon-carbon double bond. The group may be in either the cis- or trans- configuration around each double bond. In certain embodiments, the alkenyl group can have from 2 to 10 carbon atoms, in certain embodiments from 2 to 8 carbon atoms, in certain embodiments, 2 to 6 carbon atoms. The alkenyl group may be unsubstituted or substituted. Unless otherwise specified, the alkenyl group may be attached at any suitable carbon atom and, if substituted, may be substituted at any suitable carbon atom. Examples of alkenyl groups include but are not limited to ethenyl (vinyl), 2-propenyl (allyl), 1-methylethenyl, 2-butenyl, 3-butenyl and the like.

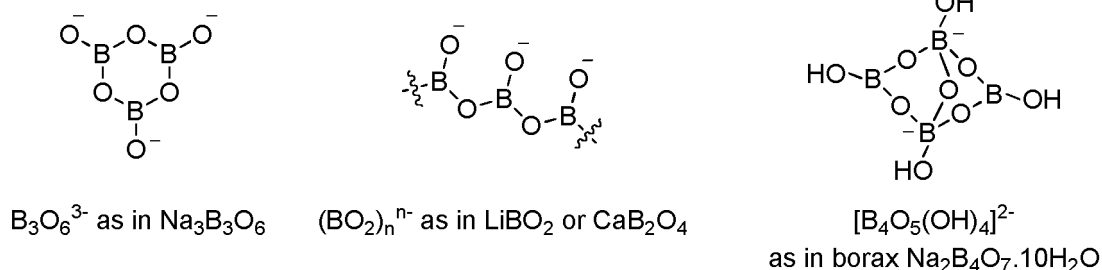
"Alkynyl" refers to a straight-chain or branched unsaturated hydrocarbon group having at least one carbon-carbon triple bond. In certain embodiments, the alkynyl group can have from 2-10 carbon atoms, in certain embodiments from 2-8 carbon atoms, in certain embodiments, 2-6 carbon atoms. The alkynyl group may be unsubstituted or substituted. Unless otherwise specified, the alkynyl group may be attached at any suitable carbon atom and, if substituted, may be substituted at any suitable

atom. Examples of alkynyl groups include but are not limited to ethynyl, prop-1-ynyl, prop-2-ynyl, 1-methylprop-2-ynyl, but-1-ynyl, but-2-ynyl, but-3-ynyl and the like.

“Aryl” refers to an aromatic carbocyclic group. The aryl group may have a single ring or multiple condensed rings. In certain embodiments, the aryl group can have from 6 to 20 carbon atoms, in certain embodiments from 6 to 15 carbon atoms, in certain embodiments, 6 to 12 carbon atoms. The aryl group may be unsubstituted or substituted. Unless otherwise specified, the aryl group may be attached at any suitable carbon atom and, if substituted, may be substituted at any suitable carbon atom. Examples of aryl groups include, but are not limited to, phenyl, naphthyl, anthracenyl and the like.

As used herein, “bath” includes a concentrate for ease of storage and transport.

“Borate ion” refers to a range of ionic compounds containing boron and oxygen. The borate ion may be a mononuclear species comprising a BO_3 or BO_4 unit, or a cyclic, linear, caged or polymeric structure formed by the linking together of BO_3 and/or BO_4 units by sharing oxygen atoms. The term “borate ion” likewise includes metaborate ions, the chemical formula for which can be written in its simplest form as BO_2 . Metaborate ions, however, appear to exist as long chains of BO_3 units sharing two oxygen atoms. Examples of borate ions are provided below:



“Cycloalkyl” refers to a cyclic saturated hydrocarbon group. In certain embodiments, the cycloalkyl group may have from 3-10 carbon atoms, in certain embodiments from 3-10 carbon atoms, in certain embodiments, 3-8 carbon atoms, in certain embodiments, 3-6 carbon atoms. The cycloalkyl group may be unsubstituted or substituted. Unless otherwise specified, the cycloalkyl group may be attached at any suitable carbon atom and, if substituted, may be substituted at any suitable atom. Typical cycloalkyl groups include but are not limited to cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl and the like.

“Heterocycloalkyl” refers to a saturated cyclic hydrocarbon group wherein one or more carbon atoms are independently replaced with one or more heteroatoms (e.g. nitrogen, oxygen, phosphorus and/or sulfur atoms). The heterocycloalkyl group may have from 2-10 carbon atoms, in certain embodiments from 2-10 carbon atoms, in certain embodiments, 2-8 carbon atoms in certain embodiment, 2-6 carbon atoms. The heterocycloalkyl group may be unsubstituted or substituted. Unless otherwise

specified, the heterocycloalkyl group may be attached at any suitable atom and, if substituted, may be substituted at any suitable atom. Examples of heterocycloalkyl group include but are not limited to epoxide, morpholinyl, piperadiny, piperazinyl, thirranly and the like.

“Heteroalkyl” refers to a straight-chain or branched saturated hydrocarbon group wherein one or more carbon atoms are independently replaced with one or more heteroatoms (e.g. nitrogen, oxygen, phosphorus and/or sulfur atoms). In certain embodiments, the heteroalkyl group may have from 1 to 10 carbon atoms, in certain embodiments from 1 to 8 carbon atoms, in certain embodiments from 1 to 6 carbon atoms. The heteroalkyl group may be unsubstituted or substituted. Unless otherwise specified, the heteroalkyl group may be attached at any suitable atom and, if substituted, may be substituted at any suitable atom.

“Heteroaryl” refers to an aromatic carbocyclic group wherein one or more carbon atoms are independently replaced with one or more heteroatoms (e.g. nitrogen, oxygen, phosphorus and/or sulfur atoms). In certain embodiments, the heteroaryl group can have from 5 to 20 carbon atoms, in certain embodiments from 5 to 15 carbon atoms, in certain embodiments, 5 to 12 carbon atoms. Unless otherwise specified, the heteroaryl group may be attached at any suitable atom and, if substituted, may be substituted at any suitable atom. Examples of heteroaryl groups include but are not limited to furanyl, indolyl, oxazolyl, pyridinyl, pyrimidinyl, thiazolyl, thiophenyl and the like.

“Heteroatom” refers to nitrogen, oxygen or sulfur, preferably nitrogen or oxygen and most preferably nitrogen.

“Room temperature” means from about 20°C to about 35°C.

“Substituted” refers to a group in which one or more (e.g. 1, 2, 3, 4 or 5) hydrogen atoms are each independently replaced with substituents which may be the same or different. Examples of substituents include but are not limited to -halo, -C(halo)₃, -R^a, =O, =S, -O-R^a, -S-R^a, -NR^aR^b, =NR^a, =N-OR^a, -CN, -SCN, -NCS, -NO₂, -C(O)-R^a, -COOR^a, -C(S)-R^a, -C(S)OR^a, -S(O)₂OH, -S(O)₂-R^a, -S(O)₂NR^aR^b, -O-S(O)-R^a and -CON^aN^b; wherein R^a and R^b are independently selected from the groups consisting of H, alkyl, aryl, arylalkyl-, heteroalkyl, heteroaryl, heteroaryl-alkyl-, or R^a and R^b together with the atom to which they are attached form a heterocycloalkyl group, and wherein R^a and R^b may be unsubstituted or further substituted as defined herein.

Detailed description

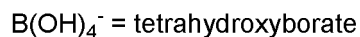
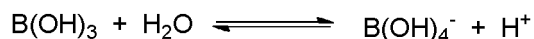
In one aspect, the present invention provides an aqueous platinum electroplating bath comprising:

- a) a source of platinum ions; and
- b) a source of borate ions.

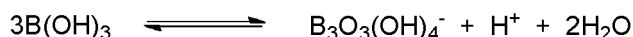
The source of platinum ions may be at least one (e.g. 1, 2, 3, 4 or 5 preferably 1) platinum plating salt or complex. The platinum plating salts useful in the invention include a large number of salts or dissolved complexes, for example, diammine dinitroplatinum(II) (i.e. "P Salt"), tetraammineplatinum(II) hydrogen orthophosphate (i.e. "Q Salt[®]"), tetraammineplatinum(II) sulphate, alkali metal hexahydroxyplatinate(IV) (such as sodium hexahydroxyplatinate(IV) or potassium hexahydroxyplatinate(IV)), alkali metal tetranitroplatinate(II) (e.g. sodium tetranitroplatinate(II) or potassium tetranitroplatinate(II)), alkali metal salts of hydrogen hexachloroplatinate(IV) (such as sodium hexachloroplatinate(IV) or potassium hexachloroplatinate(IV)), alkali metal salts of hydrogen dinitrosulphatoplatinate(II) (e.g. sodium dinitrosulphatoplatinate(II) or potassium dinitrosulphatoplatinate(II)), tetraammineplatinum(II) halides (e.g. tetraammineplatinum(II) chloride), alkali metal tetrahaloplatinates (such as sodium tetrachloroplatinate(II) or potassium tetrachloroplatinate), tetraammineplatinum(II) hydrogen carbonate, tetraammineplatinum(II) hydroxide and tetraammineplatinum(II) nitrate. The platinum ions may be cationic or anionic. The platinum ions may be may be at an oxidation state of (II) or (IV).

The bath of the present invention comprises borate ions. In one embodiment, the source of borate ions is a boron-containing acid optionally in combination with at least one borate salt. Examples of suitable boron-containing acids include but are not limited to boric acid, tetraboric acid and pyroboric acid. In one preferred embodiment, the source of borate ions is a boron-containing acid, preferably boric acid. In another preferred embodiment, the source of borate ions is a boron-containing acid (preferably boric acid) and at least one (e.g. 1, 2, 3, 4 or 5) borate salt. The use of a boron-containing acid in combination with one or more borate salts may be desirable as a buffered plating bath may be prepared.

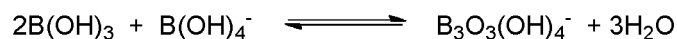
Boric acid is moderately soluble in water with a large negative heat of solution so that the solubility increases markedly with temperature ("Advanced Inorganic Chemistry", 2nd Edition, F. A. Cotton and G. Wilkinson, John Wiley & Sons, 1966). It is a very weak and exclusively monobasic acid which acts as a Lewis acid (accepting OH⁻) rather than as a proton donor.



At concentrations $\leq 0.025\text{M}$, essentially only mononuclear species B(OH)_3 and B(OH)_4^- are present. However, at higher concentrations, the acidity increases and pH measurements are consistent with the formation of polymeric species such as:



Polymers also appear to be present in mixed solutions of boric acid and borates e.g.:



In one embodiment, the at least one borate salt may be selected from the group consisting of alkali metal borates, alkaline earth metal borates and ammonium borates. Hydrates or anhydrous salts may be used, although the use of anhydrous salts is not essential as the plating bath is aqueous. When the salt is an alkali metal salt, the salt is preferably a lithium, sodium or potassium salt. When the salt is an alkaline earth metal salt, the salt is preferably a magnesium or calcium salt. Examples of suitable borate salts include but are not limited to metaborates, tetraborates, diborates and pentaborates, such as lithium metaborate (LiBO_2), lithium metaborate dihydrate ($\text{LiBO}_2 \cdot 2\text{H}_2\text{O}$), sodium metaborate (NaBO_2), sodium metaborate hydrate ($\text{NaBO}_2 \cdot x\text{H}_2\text{O}$), calcium metaborate [$\text{Ca}(\text{BO}_2)_2$], calcium metaborate dihydrate [$\text{Ca}(\text{BO}_2)_2 \cdot 2\text{H}_2\text{O}$], sodium tetraborate ($\text{Na}_4\text{B}_4\text{O}_7$), sodium tetraborate decahydrate ($\text{Na}_4\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), potassium tetraborate ($\text{K}_4\text{B}_4\text{O}_7$), potassium tetraborate tetrahydrate ($\text{K}_4\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$), ammonium diborate [$(\text{NH}_4)_2\text{B}_4\text{O}_7$], ammonium diborate tetrahydrate [$(\text{NH}_4)_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$], potassium diborate [$\text{K}_2\text{B}_4\text{O}_7$], potassium diborate tetrahydrate [$\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$], ammonium pentaborate octahydrate [$(\text{NH}_4)_2\text{B}_{10}\text{O}_{16} \cdot 8\text{H}_2\text{O}$].

In another embodiment, the source of borate ions may be a metaborate salt optionally in combination with at least one other borate salt. In one preferred embodiment, the source of borate ions is a metaborate salt, such as an alkali metal (e.g. sodium or potassium), alkaline earth metal (e.g. calcium) or ammonium metaborate. In another preferred embodiment, the source of borate ions is a metaborate salt in combination with at least one (e.g. 1, 2, 3, 4 or 5) other borate salt. Suitable metaborate and borate salts are as given above.

The plating baths when made up to be ready for use suitably have a borate ion concentration of about 0.1 to about 90 g/litre. While it is possible for the borate ion concentration to be greater than about 90 g/litre, this is usually undesirable as the borate may begin to crystallise out of the plating bath at lower temperatures, e.g. room temperature. This may then create handling or processing difficulties with regard to the plating bath. In some embodiments, the borate ion concentration is about ≥ 0.1 g/litre. In some embodiments, the borate ion concentration is about ≥ 1 g/litre. In some embodiments, the borate ion concentration is about ≥ 2.5 g/litre. In some embodiments, the borate ion concentration is about ≥ 5 g/litre. In some embodiments, the borate ion concentration is about ≥ 10 g/litre. In some embodiments, the borate ion concentration is about ≤ 85 g/litre, in some embodiments about ≤ 80 g/litre, in some embodiments about ≤ 75 g/litre, in some embodiments about ≤ 70 g/litre, in some embodiments about ≤ 65 g/litre, in some embodiments about ≤ 60 g/litre, in some embodiments about ≤ 55 g/litre, in some embodiments about ≤ 50 g/litre, in some embodiments about ≤ 45 g/litre, in some embodiments about ≤ 40 g/litre, in some embodiments about ≤ 35 g/litre, in some embodiments about ≤ 30 g/litre, in some embodiments about ≤ 25 g/litre, in some embodiments about ≤ 20 g/litre. In one preferred embodiment, the borate ion concentration is about 5 to about 30 g/litre. In the first instance, the borate ion concentration may be determined from the mass of the components used to make up

the bath. However, when the bath is in use, the borate ion concentration may be assessed using analytical techniques such as titration, gravimetric methods or ion-chromatography.

The platinum plating bath when it is ready for use or in use has a pH in the range from about 2 to about 14. If the pH of the bath is <2, the bath may be very corrosive which may present equipment problems with its use and containment. For example, the equipment needed to analyse the bath (e.g. HPLC internals and column) may be severely affected, or levellers (if used) or other organic additives (if used), such as wetting agents may be destroyed. Moreover, the range of substrates which may be plated would be limited, as well as the materials used in supporting the workpiece. In certain embodiments, the pH is ≥ 2 , in certain embodiments ≥ 2.5 , in certain embodiments ≥ 3 , in certain embodiments ≥ 3.5 , in certain embodiments ≥ 4 , in certain embodiments ≥ 4.5 , in certain embodiments ≥ 5 , in certain embodiments ≥ 5.5 , in certain embodiments ≥ 6 , in certain embodiments ≥ 6.5 , in certain embodiments ≥ 7 , in certain embodiments ≥ 7.5 . In certain embodiment, the pH is ≤ 14 , in certain embodiments ≤ 13.5 , in certain embodiments ≤ 13 , in certain embodiments ≤ 12.5 , in certain embodiments ≤ 12 , in certain embodiments ≤ 11.5 , in certain embodiments ≤ 11 , in certain embodiments ≤ 10.5 , in certain embodiments ≤ 10 , in certain embodiments ≤ 9.5 , in certain embodiments ≤ 9 , in certain embodiments ≤ 8.5 , in certain embodiments ≤ 8 . In one embodiment, the pH is from about 6 to about 9. A bath having a pH of from about 7 to about 9 may be termed a "neutral" bath and is an example of a non-corrosive plating bath. A neutral bath may be desirable as there is little bubbling at the cathode as most energy is used in plating. In another embodiment, the pH is from about 2 to about 7. A bath having a pH of from about 2 to about 7 may be termed an "acid" bath. An acid bath may be desirable as the surface to be plated is less likely to be oxidised and because of this, adhesion of the applied electroplate can be improved.

The pH of the plating bath may be adjusted by the addition of suitable acids, bases or a mixture thereof. For example, "Q Salt[®]" solution is normally supplied for use at about pH 10 to 11 and the addition of acid is required to lower the pH of the solution. Any suitable inorganic acid, organic acid or mixture thereof may be utilised. Examples of suitable organic acids include but are not limited to formic acid, acetic acid and oxalic acid. Examples of suitable inorganic acids include but are not limited to hydrohalic acids (e.g. HCl, HBr or HI), sulfur-containing acids (e.g. sulphuric acid), phosphorus-containing acids (such as hypophosphoric acid (H_3PO_2), phosphorous acid (H_3PO_3), ortho-phosphoric acid (H_3PO_4)) and boron-containing acids.

Any suitable inorganic base, organic base or mixture may be utilised to increase the pH of the plating bath, if this is required. Examples of suitable inorganic bases include but are not limited to alkali metal hydroxides, alkaline earth metal hydroxides, alkali metal carbonates, alkali metal phosphates and alkali metal silicates, such as potassium hydroxide, sodium hydroxide, calcium hydroxide, magnesium hydroxide, sodium carbonate, potassium carbonate, sodium phosphate, potassium phosphate, sodium silicate, potassium silicate. Examples of suitable organic bases include but are

not limited to amines and tetraalkyl ammonium hydroxides, such as ammonia, ethanolamine or choline hydroxide.

When a borate salt such as those described above is used, the borate salt itself may act as a base.

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The pH will change slowly as the platinum is plated from the bath. The concentration of the platinum can be maintained in the bath by adding fresh plating solution that comprises the platinum ions, borate ions, acid (if used) and base (if used). Alternatively, each component may be added individually. Desirably, the plating bath is analysed regularly and replenished as necessary in order to maintain the desired concentration of each component. Suitable concentrations for e.g. the platinum ions and/or borate ions when the bath is in use are generally those provided above and below in respect of when the bath is ready for use.

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The platinum ions and the borate ions may be obtained from different sources. For example, as described above, the platinum ions may be derived from the platinum plating salts and complexes, and the borate ions may be derived from a boron-containing acid optionally in combination with one or more borate salts or, a metaborate salt optionally in combination with one or more other metaborate salts.

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In another embodiment, the source of platinum ions and the source of borate ions may be obtained from the same source. In this embodiment, the source for both may be a platinum borate salt or complex.

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For certain platinum electroplating applications, the use of sulfur-containing materials may not be desirable. An example where sulfur-containing materials may not be desirable is the platinum plating of materials for aerospace applications, especially turbine blades. Accordingly, plating baths containing materials such as sulfur-containing platinum plating salts or complexes, or sulfur-containing acids may not be optimal for such applications. In one embodiment, therefore, the aqueous platinum plating bath does not comprise a sulfur-containing platinum plating salt or complex.

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In another embodiment, the aqueous platinum plating bath does not comprise a sulfur-containing acid (if used).

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However, the use of sulfur-containing materials may be suitable for the platinum plating of materials other than for aerospace applications.

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In other electroplating applications, it may be desirable to avoid the use of halogen-containing materials, particularly chlorine-containing materials, as they may cause sensitization. In this instance, it may be desirable to use a platinum salt or complex which does not comprise halide ions and to select an acid (if used) which is not a hydrohalic acid.

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The plating baths when made up to be ready for use suitably have a platinum ion concentration of about 1 to about 30 g/litre. Preferred platinum concentrations depend upon the product to be coated and the coating apparatus but are typically about 5 g/litre to about 20 g/litre for most normal operations. In some embodiments, the platinum ion concentration is ≥ 5 g/litre, for example, ≥ 7 g/litre.

5 In some embodiments, the platinum ion concentration is ≥ 10 g/litre, for example, ≥ 15 g/litre. In some embodiments, the platinum ion concentration is ≤ 20 g/litre, for example, ≤ 15 g/litre.

The plating bath of the present invention may be used at temperatures from about room temperature to about 100°C . In certain embodiments, the temperature may be from about 60°C to about 100°C , in
10 certain embodiments from about 60°C to about 95°C , in certain embodiments from about 70°C to about 95°C , in certain embodiments from about 75°C to about 95°C , in certain embodiments from about 75°C to about 90°C , in certain embodiments from about 70°C to about 90°C . In general, it has been found that the higher the plating temperature, the greater the plating rate. Greater loss of water by evaporation at higher temperatures may occur, however, this may be monitored and adjusted as
15 appropriate through the addition of water to the bath.

The bath of the invention may be used successfully under broadly conventional conditions and current densities. For example, the current density may be from about 1 to about $25\text{mA}/\text{cm}^2$, for example, from about 2 to about $10\text{mA}/\text{cm}^2$, such as from about 2 to about $6\text{mA}/\text{cm}^2$, e.g. about $4\text{mA}/\text{cm}^2$.
20 The bath can be used to plate using complex methods such as pulse plating or impressed AC or other interrupted plating techniques, but direct current electroplating is preferred.

The aqueous platinum electroplating bath is suitable for use in an industrial or commercial electroplating process. The bath of the present invention may be used to rapidly coat large substrates
25 in an industrial sized tank in a continual process rather than being restricted to a research tool explored by cyclic voltammetry, or by other electrochemical probing techniques in a small cell, whilst confined to a small cell. Accordingly, the rate at which the platinum is plated out of solution should be such that the process is commercially viable. In one embodiment, therefore, the rate of plating is about ≥ 0.5 microns thickness of platinum per hour. In another embodiment, the rate of plating is
30 about ≥ 1 microns thickness of platinum per hour. In yet another embodiment, the rate of plating is about ≥ 1.5 microns thickness of platinum per hour. In another embodiment, the rate of plating is about ≥ 2 microns thickness of platinum per hour. In yet another embodiment, the rate of plating is about ≥ 2.5 microns thickness of platinum per hour. In another embodiment, the rate of plating is about ≥ 3 microns thickness of platinum per hour. In yet another embodiment, the rate of plating is
35 about ≥ 3.5 microns thickness of platinum per hour. In another embodiment, the rate of plating is about ≥ 4 microns thickness of platinum per hour. In yet another embodiment, the rate of plating is about ≥ 4.5 microns thickness of platinum per hour. In another embodiment, the rate of plating is about ≥ 5 microns thickness of platinum per hour. In yet another embodiment, the rate of plating is about ≥ 5.5 microns thickness of platinum per hour. In another embodiment, the rate of plating is
40 about ≥ 6 microns thickness of platinum per hour. In yet another embodiment, the rate of plating is

about ≥ 6.5 microns thickness of platinum per hour. In another embodiment, the rate of plating is about ≥ 7 microns thickness of platinum per hour. In yet another embodiment, the rate of plating is about ≥ 7.5 microns thickness of platinum per hour. In another embodiment, the rate of plating is about ≥ 8 microns thickness of platinum per hour. In yet another embodiment, the rate of plating is about ≥ 8.5 microns thickness of platinum per hour. In another embodiment, the rate of plating is about ≥ 9 microns thickness of platinum per hour. In yet another embodiment, the rate of plating is about ≥ 9.5 microns thickness of platinum per hour. In another embodiment, the rate of plating is about ≥ 10 microns thickness of platinum per hour. In one preferred embodiment, the rate of plating is from about 5 microns thickness of platinum per hour to about 10 microns thickness per hour. When the plating bath comprises one or more other plating salts or complexes (which are not platinum plating salts or complexes), the above embodiments relate to the plating rate and thickness of platinum alloy per hour.

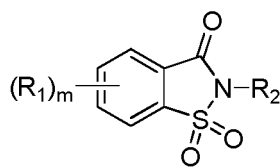
Deposition of platinum onto shaped parts may give an uneven thickness of platinum in some electroplating systems. While this can be alleviated by the use of a shaped anode to modify the electric field around the part and thereby moderate the extremes of field which cause uneven distribution, it is nevertheless desirable to find an alternative way of producing an even deposit. The platinum electroplating bath of the present invention therefore may further comprise at least one leveller. In certain embodiments, the leveller may contribute to the production of a bright or shiny plate. In certain embodiments, the leveller may contribute to the lustre of the produced plate. In certain embodiments, the leveller may help to generate a plate with increased hardness.

In one embodiment, the leveller comprises at least one unsaturated carbon-carbon or unsaturated carbon-heteroatom bond.

Preferably, the leveller is selected from the group consisting of at least one:

- a) substituted or unsubstituted saccharine or salt thereof;
- b) substituted or unsubstituted benzopyranone;
- c) substituted or unsubstituted benzaldehyde or derivative thereof;
- d) substituted or unsubstituted alkene provided the alkene is not ethylene;
- e) substituted or unsubstituted alkyne provided the alkyne is not acetylene;
- f) substituted or unsubstituted alkylnitrile;
- g) substituted or unsubstituted pyridine or addition salt thereof;
- h) substituted or unsubstituted triazole; and
- i) substituted or unsubstituted pyridinium salt.

The leveller may be a substituted or unsubstituted saccharine or salt thereof. In one preferred embodiment, therefore, the leveller is a compound of formula (1) or salts thereof:



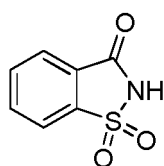
(1)

wherein m is 0, 1, 2, 3 or 4;

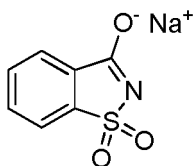
each R₁ is independently an unsubstituted C₁-C₁₀ alkyl group;

- 5 R₂ is selected from the group consisting of H, unsubstituted C₁-C₁₀ alkyl, an alkali metal ion and an alkaline earth metal ion.

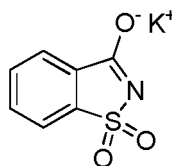
In one preferred embodiment, m is 0 i.e. the aryl group is unsubstituted. In another preferred embodiment, R₂ is H. In yet another preferred embodiment, the compound of formula (1) is a salt wherein R₂ is an alkali metal cation or an alkaline earth metal cation e.g. Na⁺, K⁺ or Ca²⁺. Examples of compounds of formula (1) include but are not limited to saccharine, sodium saccharine, potassium saccharine and calcium saccharine.



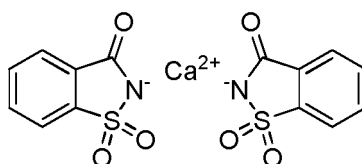
Saccharine



Sodium saccharine



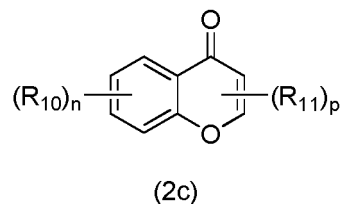
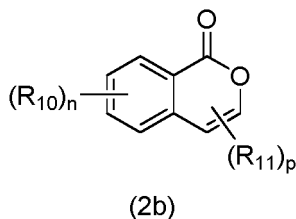
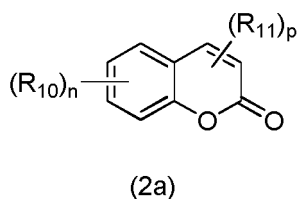
Potassium saccharine



Calcium saccharine

When the compound of formula (1) is a salt, the anionic sulfobenzimide group may be present as an amido tautomer (for example see the structure of calcium saccharine above) and/or as the iminyl tautomer (for example see the structure of sodium and potassium saccharine above). The amido and iminyl tautomers are included within the definition of the compound of formula (1).

When the leveller is a substituted or unsubstituted benzopyranone, the benzopyranone may be a substituted or unsubstituted 1-benzopyran-2-one, 2-benzopyran-1-one or 1-benzopyran-4-one. In one preferred embodiment, the leveller is a compound of formula (2a), (2b) or (2c):



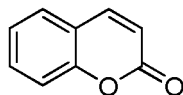
wherein n is 0, 1, 2, 3 or 4;

p is 0, 1 or 2;

- 5 each R_{10} and R_{11} is independently selected from an unsubstituted C_1 - C_{10} alkyl group.

In one embodiment, the leveller is a compound of formula (2a). In another embodiment, the leveller is a compound of formula (2b). In yet another embodiment, the leveller is a compound of formula (2c).

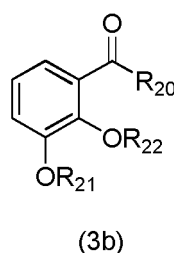
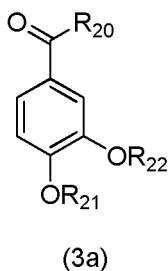
- 10 In one preferred embodiment, n is 0 i.e. the aryl group is unsubstituted. In another preferred embodiment, p is 0. An example of a compound of formula (2a) includes but is not limited to coumarin.



Coumarin

15

The leveller may be a substituted or unsubstituted benzaldehyde or derivative thereof. In one preferred embodiment, the leveller is a compound of formula (3a) or (3b):



20

wherein R_{20} is selected from the group consisting of H and $-OR_{23}$; and

R_{21} and R_{22} are independently selected from the group consisting of H, $-C(O)R_{24}$ and unsubstituted C_1 - C_{10} -alkyl; and

R_{23} and R_{24} are independently selected from the group consisting of H and unsubstituted C_1 - C_{10} -alkyl.

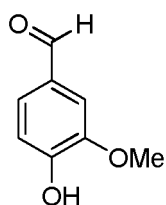
25

In one embodiment, the leveller is a compound of formula (3a). In another embodiment, the leveller is a compound of formula (3b).

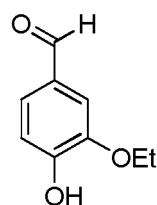
Preferably, R_{20} is selected from the group consisting of H, -OH, -OMe, -OEt, -OPr (n- or i-) and -OBu (n-, i- or t-) and more preferably, H, -OH and -OMe. In this instance, therefore, R_{23} is preferably -H, -Me, -Et, -Pr (n- or i-), -Bu (n-, i- or t-) and more preferably -H or -OMe.

5 Preferably, each R_{21} and R_{22} is independently selected from the group consisting of H, methyl, ethyl, propyl (n- or i-), butyl (n-, i- or t-), -C(O)H, -COMe, -COEt, -COPr (n- or i-) and -COBu (n-, i- or t-). More preferably, each R_{21} and R_{22} is independently selected from the group consisting of H, methyl, ethyl and -COMe. In these cases, R_{24} is preferably H, methyl, ethyl, propyl (n- or i-), butyl (n-, i- or t-) and more preferably Me.

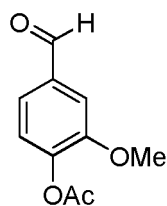
10 Examples of compounds of formula (3a) include but are not limited to vanillin, ethyl vanillin, vanillin acetate, vanillic acid and methyl vallinate. Examples of compounds of formula (3b) include but are not limited to ortho-vanillin and 3-methoxysalicylic acid.



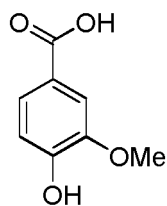
Vanillin



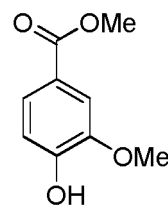
Ethyl vanillin



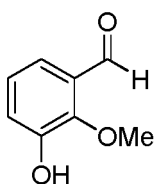
Vanillin acetate



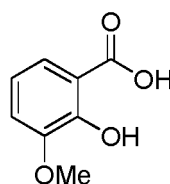
Vanillic acid



Methyl vallinate

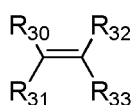


Ortho-vanillin



3-Methoxysalicylic acid

20 The leveller may be a substituted or unsubstituted alkene. In this instance, it is preferred that the leveller is not ethylene. In one preferred embodiment, the leveller is a compound of formula (4):



(4)

wherein each R_{30} , R_{31} , R_{32} and R_{33} is independently selected from the group consisting of H, unsubstituted C_1 - C_{10} -alkyl, substituted C_1 - C_{10} -alkyl, $-\text{CO}_2R_{34}$, $-\text{NR}_{34}R_{35}$, $-\text{CONR}_{34}R_{35}$ and $-\text{CN}$, provided that R_{30} , R_{31} , R_{32} and R_{33} are not all H,

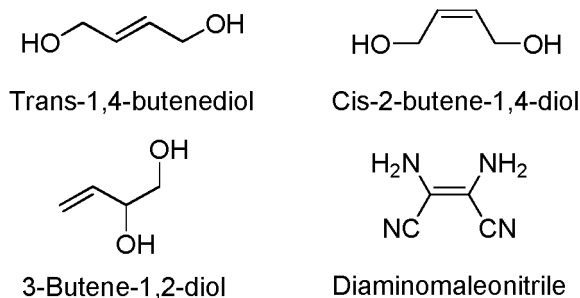
wherein the substituents are selected from the group consisting of at least one (e.g. 1, 2, 3, 4 or 5) - OH, $-\text{CO}_2R_{36}$, $-\text{OC(O)}R_{36}$, $-\text{NR}_{36}R_{37}$, $-\text{CONR}_{36}R_{37}$, $-\text{CN}$, $-\text{SO}_3^-\text{Na}^+$ and $-\text{SO}_3^-\text{K}^+$;

R_{34} and R_{35} are independently selected from the group consisting of H and unsubstituted C_1 - C_{10} -alkyl; and

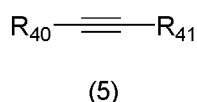
R_{36} and R_{37} are independently selected from the group consisting of H and unsubstituted C_1 - C_{10} -alkyl.

The compounds of formula (4) may be cis-, trans- or geminal-alkenyl compounds. When the compound of formula (4) is cis-, R_{30} and R_{32} or R_{31} and R_{33} are H. When the compound of formula (4) is trans-, R_{30} and R_{33} or R_{31} and R_{32} are H. When the compound of formula (4) is geminal-, R_{30} and R_{31} or R_{32} and R_{33} are H. Alternatively, R_{30} , R_{31} , R_{32} and R_{33} may each be substituted with a group other than H.

Preferably, each R_{30} , R_{31} , R_{32} and R_{33} is independently selected from the group consisting of H, unsubstituted C_1 - C_{10} -alkyl, substituted C_1 - C_{10} -alkyl, $-\text{NH}_2$ and $-\text{CN}$. Preferably, the substituents are selected from the group consisting of at least one (e.g. 1, 2, 3, 4 or 5) $-\text{OH}$, $-\text{OC(O)Me}$, $-\text{NH}_2$, $-\text{CN}$ and $-\text{SO}_3^-\text{Na}^+$ and $-\text{SO}_3^-\text{K}^+$. More preferably, each R_{30} , R_{31} , R_{32} and R_{33} is independently selected from the group consisting of H, $-\text{CH}_2\text{-OH}$, $-\text{CH(OH)CH}_2\text{-OH}$, $-\text{NH}_2$ and $-\text{CN}$. Examples of compounds of formula (4) include but are not limited to butenediol (e.g. trans-1,4-butenediol, cis-2-butene-1,4-diol, or 3-butene-1,2-diol) and diaminomaleonitrile.



The leveller may be a water-soluble substituted or unsubstituted C_2 - C_{10} -alkyne provided the alkyne is not acetylene. In a preferred embodiment, the leveller is a compound of formula (5):

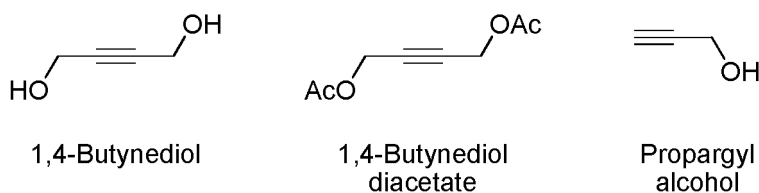


wherein R_{40} and R_{41} are independently selected from the group consisting of H, unsubstituted C_1 - C_{10} -alkyl and substituted C_1 - C_{10} -alkyl, provided that R_{40} and R_{41} are not both H,

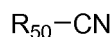
wherein the substituents are selected from the group consisting of at least one (e.g. 1, 2, 3, 4 or 5) of -OH, -CO₂R₄₂, -OC(O)R₄₂, -NR₄₂R₄₃, -CONR₄₂R₄₃, -CN, -SO₃⁻Na⁺ and -SO₃⁻K⁺;

R₄₂ and R₄₃ are independently selected from the group consisting of H and unsubstituted C₁-C₁₀-alkyl.

- 5 Preferably, R₄₀ and R₄₁ are independently selected from the group consisting of H, unsubstituted C₁-C₁₀-alkyl and substituted C₁-C₁₀-alkyl, wherein the substituents are selected from the group consisting of at least one (e.g. 1, 2, 3, 4 or 5) of -OH, OC(O)Me, -NH₂, -CN, -SO₃⁻Na⁺ and -SO₃⁻K⁺. More preferably, R₄₀ and R₄₁ are independently selected from the group consisting of H, -CH₂-OH, -CH(OH)CH₂-OH and -CH₂OC(O)Me. Examples of compounds of formula (5) include but are not
10 limited to 1,4-butyne-1,3-diol, 1,4-butyne-1,3-diol diacetate and propargyl alcohol.



- When the leveller is a substituted or unsubstituted alkylnitrile, it is preferred that the leveller is a
15 compound of formula (6):



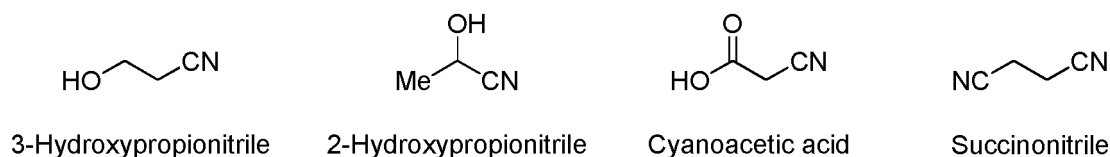
(6)

- wherein R₅₀ is a substituted or unsubstituted C₁-C₁₀-alkyl, and the substituents are selected from the
20 group consisting of at least one (e.g. 1, 2, 3, 4 or 5) of -OR₅₁, -CO₂R₅₁, -OC(O)R₅₁, -NR₅₁R₅₂ and -CN; and

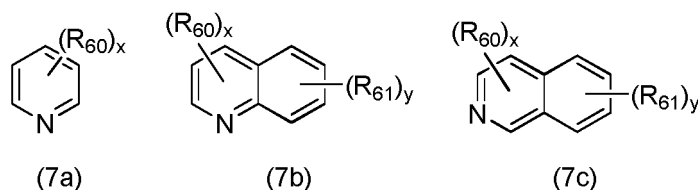
wherein R₅₁ and R₅₂ are independently selected from the group consisting of H and unsubstituted C₁-C₁₀-alkyl.

- 25 Preferably, R₅₀ is a substituted or unsubstituted C₁-C₁₀-alkyl, wherein the substituents are selected from the group consisting of at least one (e.g. 1, 2, 3, 4 or 5) of -OH, -OMe, -OPr (n- or i-), -OBu (n-, i- or t-), -CO₂H, -NH₂ and -CN. More preferably, R₅₀ is selected from the group consisting of -CH₂CH₂-OH, -CH(OH)-CH₃, -CH₂CO₂H and -CH₂-CH₂-CN. Examples of compounds of formula (6) include but are not limited to 3-hydroxypropionitrile, 2-hydroxypropionitrile, cyanoacetic acid and succinonitrile

30



In another embodiment, the leveller may be a substituted or unsubstituted pyridine or an addition salt thereof. Preferably, the leveller is a compound of formula (7a), (7b) or (7c):



5

wherein R_{60} and R_{61} are independently selected from the group consisting of $-OH$, $-CN$, $-CONR_{62}R_{63}$, $-CO_2R_{62}$, $-COR_{63}$, $-N$ -(unsubstituted C_1 - C_{10} -alkyl)-pyrrolidinyl, unsubstituted C_1 - C_{10} -alkyl, substituted C_1 - C_{10} -alkyl, unsubstituted C_2 - C_{10} -alkenyl, substituted C_2 - C_{10} -alkenyl, $-SO_2-R_{63}$, $-N=N$ -(unsubstituted C_6 - C_{10} -aryl), $-N=N$ -(substituted C_6 - C_{20} -aryl), unsubstituted pyridyl, substituted pyridyl,

10 wherein the substituents are independently selected from the group consisting of at least one (e.g. 1, 2, 3, 4 or 5) of $-CN$, $-CONR_{64}R_{65}$, $-COR_{65}$, $-CO_2R_{64}$, $-OH$, $-NR_{64}R_{65}$ and $=NR_{64}$;

R_{62} is selected from the group consisting of H , $-OH$ and unsubstituted C_1 - C_{10} -alkyl;

R_{63} is selected from the group consisting of H , $-OH$, unsubstituted C_1 - C_{10} -alkyl, unsubstituted C_1 - C_{10} -alkyl- CO_2H , $-NH_2$, $-NH$ -(unsubstituted C_1 - C_{10} -alkyl), $-N$ -(unsubstituted C_1 - C_{10} -alkyl) $_2$;

15 R_{64} is selected from the groups defined for R_{62} ;

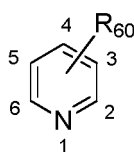
R_{65} is selected from the groups defined for R_{63} ;

each x is 0, 1, 2 or 3; and

each y is 0, 1, 2, 3 or 4.

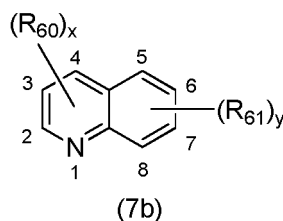
20 In one embodiment, the leveller is a compound of formula (7a). In another embodiment, the leveller is a compound of (7b). In yet another embodiment, the leveller is a compound of (7c).

In one embodiment, the compound of formula (7a) is unsubstituted i.e. x is 0. In another embodiment, x is 1 i.e. the compound (7a) is monosubstituted. In this instance, the substituent R_{60} may be
 25 attached to any one of the carbons in the pyridine ring i.e. at C-2, C-3 or C-4. In another embodiment, x is 2 for the compound of (7a) i.e. the compound is disubstituted. In this instance, each substituent R_{60} may be the same or different. The substituents may be attached to any of the carbons in the pyridine ring i.e. the compound (7a) may be 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, 3,5- or 3,6-disubstituted. In another embodiment, compound (7a) is trisubstituted i.e. x is 3. In this instance, each substituent R_{60}
 30 may be the same or different. The substituents may be attached to any of the carbons in the pyridine ring i.e. the compound (7a) may be 2,3,4-, 2,3,5-, 2,3,6-, 2,4,5-, 2,4,6-, 3,4,5- or 3,4,6-trisubstituted.



(7a)

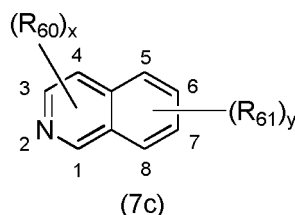
In one embodiment, x may be 0, 1, 2 or 3 for the compound of formula (7b). When x is 0, the pyridinyl ring is unsubstituted. In another embodiment, when x is 1, the R_{60} substituent may be attached at any of the carbon atoms at C-2, C-3 or C-4. In yet another embodiment, when x is 2, each R_{60} substituent may be the same or different. The substituents may be attached to any of the carbons in the pyridine ring i.e. the compound (7b) may be 2,3-, 2,4- or 3,4-substituted. In another embodiment, x is 3 and each R_{60} is attached at C-2, C-3 and C-4. In this instance, each substituent R_{60} may be the same or different.



In another embodiment, y may be 0, 1, 2, 3 or 4 for the compound (7b). In one embodiment, y is 0. In yet another embodiment, y is 1. In this instance, the substituent R_{61} may be attached to any of the carbon atoms at C-5, C-6, C-7 or C-8. In yet another embodiment, when y is 2, each R_{61} substituent may be the same or different. The substituents may be attached in any substitution pattern to any of the carbons at C-5, C-6, C-7 or C-8 i.e. the compound (7b) may be 5,6-, 5,7-, 5,8-, 6,7-, 6,8- or 7,8-substituted. In another embodiment, when y is 3, each R_{61} substituent may be the same or different. The substituents may be attached in any combination to the carbons at C-5, C-6, C-7 or C-8 i.e. the compound (7b) may be 5,6,7-, 5,6,8-, 5,7,8- or 6,7,8-substituted. In another embodiment, y is 4 and each R_{61} is attached at C-5, C-6, C-7 and C-8. In this instance, each substituent R_{61} may be the same or different.

In one embodiment, x and y are 0 i.e. compound (7b) is quinoline.

In one embodiment, x may be 0, 1, 2 or 3 for the compound of formula (7c). When x is 0, the pyridinyl ring is unsubstituted. In another embodiment, when x is 1, the R_{60} substituent may be attached at any of the carbon atoms at C-1, C-3 or C-4. In yet another embodiment, when x is 2, each R_{60} substituent may be the same or different. The substituents may be attached to any of the carbons in the pyridine ring i.e. the compound (7c) may be 1,3-, 1,4- or 3,4-substituted. In another embodiment, x is 3 and each R_{60} is attached at C-1, C-3 and C-4. In this instance, each substituent R_{60} may be the same or different.



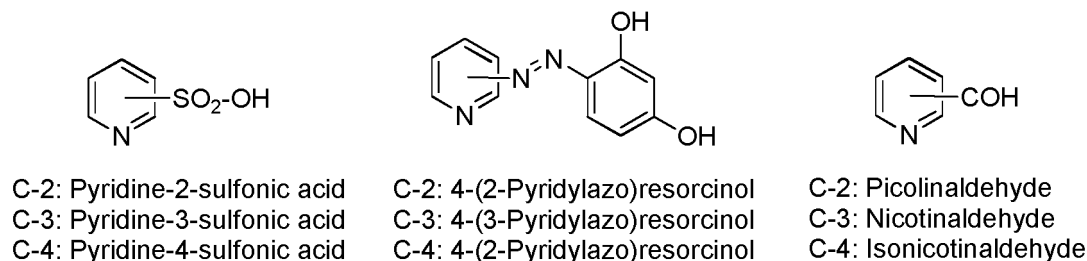
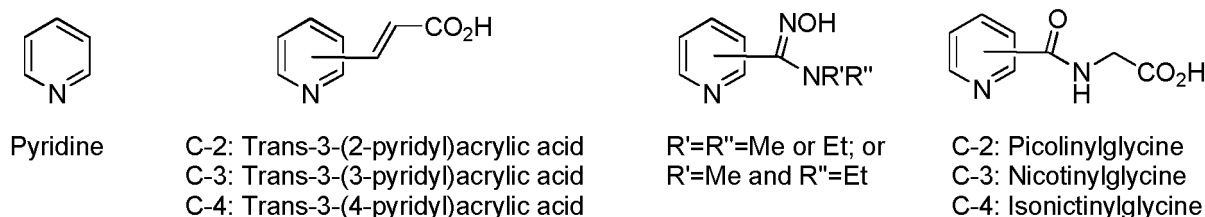
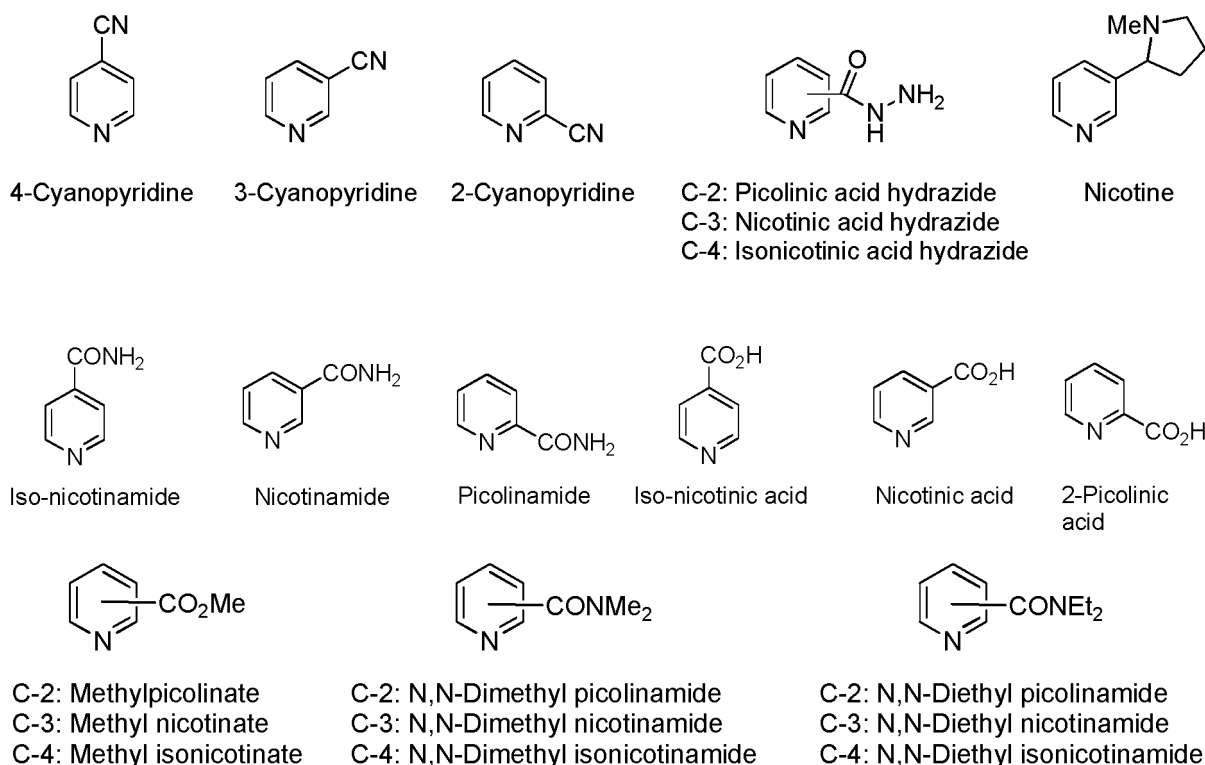
In another embodiment, y may be 0, 1, 2, 3 or 4 for the compound (7c). In one embodiment, y is 0. In yet another embodiment, y is 1. In this instance, the substituent R_{61} may be attached to any of the carbon atoms at C-5, C-6, C-7 or C-8. In yet another embodiment, when y is 2, each R_{61} substituent may be the same or different. The substituents may be attached in any combination to any of the carbons at C-5, C-6, C-7 or C-8 i.e. the compound (7c) may be 5,6-, 5,7-, 5,8-, 6,7-, 6,8- or 7,8-substituted. In another embodiment, when y is 3, each R_{61} substituent may be the same or different. The substituents may be attached in any combination to the carbons at C-5, C-6, C-7 or C-8 i.e. the compound (7c) may be 5,6,7-, 5,6,8-, 5,7,8- or 6,7,8-substituted. In another embodiment, y is 4 and each R_{61} is attached at C-5, C-6, C-7 and C-8. In this instance, each substituent R_{61} may be the same or different.

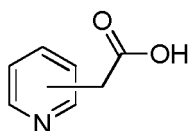
In one embodiment, x and y is 0 i.e. compound (7c) is isoquinoline.

Preferably, R_{60} is selected from the group consisting of $-\text{OH}$, $-\text{CN}$, $-\text{CONR}_{62}\text{R}_{63}$, $-\text{CO}_2\text{R}_{62}$, $-\text{COR}_{63}$, N -(unsubstituted $\text{C}_1\text{-C}_{10}$ -alkyl)-pyrrolidinyl, unsubstituted $\text{C}_1\text{-C}_{10}$ -alkyl, substituted $\text{C}_2\text{-C}_{10}$ -alkenyl, $-\text{SO}_2\text{R}_{63}$, $-\text{N}=\text{N}$ -(substituted $\text{C}_6\text{-C}_{20}$ -aryl) and unsubstituted pyridyl. Preferably, the substituents are selected from the group consisting of at least one (e.g. 1, 2, 3, 4 or 5) $-\text{CN}$, $-\text{CONH}_2$, $-\text{CONHMe}$, $-\text{CONH}^t\text{Et}$, $-\text{CONMe}_2$, $-\text{CONEt}_2$, $-\text{COH}$, $-\text{CO}_2\text{H}$, $-\text{CO}_2\text{Me}$, $-\text{CO}_2\text{Et}$, $-\text{OH}$, $-\text{NH}_2$, $=\text{N-OH}$, $-\text{NMe}_2$, $-\text{NEt}_2$, $-\text{NMeEt}$. R_{62} and R_{64} are preferably independently selected from the group consisting of H , $-\text{OH}$, methyl, ethyl, propyl (n - or i -) and butyl (n -, i - or t -). R_{63} and R_{65} are preferably independently selected from the group consisting of H , $-\text{OH}$, methyl, ethyl, propyl (n - or i -), butyl (n -, i - or t -), $-\text{NH}_2$, $-\text{NHMe}$, $-\text{NH}^t\text{Et}$, $-\text{NHPr}$ (n - or i -), $-\text{NHBu}$ (n -, i - or t -), $-\text{NMe}_2$, $-\text{NEt}_2$, $-\text{NPr}_2$ (wherein each Pr group is independently n - or i -), $-\text{NBu}_2$ (wherein each Bu group is independently n -, i - or t -) and $-\text{CH}_2\text{-CO}_2\text{H}$. In one preferred embodiment, R_{60} is selected from the group consisting of methyl, ethyl, propyl (n - or i -), butyl (n -, i - or t -), $-\text{CN}$, $-\text{CO}_2\text{H}$, $-\text{COH}$, $-\text{CONH}(\text{OH})$, $-\text{CONH}(\text{NH}_2)$, $-\text{CONH}_2$, N -Me-pyrrolidinyl-2-yl, $-\text{CO}_2\text{Me}$, $-\text{CONMe}_2$, $-\text{CO}_2\text{Et}$, $-\text{CONEt}_2$, $-\text{CONMeEt}$, $-\text{C}=\text{C-CO}_2\text{H}$, $-\text{SO}_2\text{OH}$, $-\text{N}=\text{N}$ -(2,4-dihydroxy-phenyl), $-\text{pyridyl}$, $-\text{C}(\text{NOH})(\text{NH}_2)$, $-\text{C}(\text{NOH})(\text{NMe}_2)$, $-\text{C}(\text{NOH})(\text{NEt}_2)$, $-\text{C}(\text{NOH})(\text{NMeEt})$ and $-\text{CONH}(\text{CH}_2\text{CO}_2\text{H})$. In one preferred embodiment, R_{61} is selected from the group consisting of methyl, ethyl, propyl (n - or i -), butyl (n -, i - or t -), $-\text{CN}$, $-\text{CO}_2\text{H}$, $-\text{COH}$, $-\text{CONH}(\text{OH})$, $-\text{CONH}(\text{NH}_2)$, $-\text{CONH}_2$, N -Me-pyrrolidinyl-2-yl, $-\text{CO}_2\text{Me}$, $-\text{CONMe}_2$, $-\text{CO}_2\text{Et}$, $-\text{CONEt}_2$, $-\text{CONMeEt}$, $-\text{C}=\text{C-CO}_2\text{H}$, $-\text{SO}_2\text{OH}$, $-\text{N}=\text{N}$ -(2,4-dihydroxy-phenyl), $-\text{pyridyl}$, $-\text{C}(\text{NOH})(\text{NH}_2)$, $-\text{C}(\text{NOH})(\text{NMe}_2)$, $-\text{C}(\text{NOH})(\text{NEt}_2)$, $-\text{C}(\text{NOH})(\text{NMeEt})$ and $-\text{CONH}(\text{CH}_2\text{CO}_2\text{H})$. In another preferred embodiment, R_{61} is selected from the group consisting of methyl, ethyl, propyl (n - or i -), butyl (n -, i - or t -), $-\text{CN}$, $-\text{CO}_2\text{H}$, $-\text{COH}$, $-\text{CONH}(\text{OH})$, $-\text{CONH}(\text{NH}_2)$, $-\text{CONH}_2$, $-\text{CONH}(\text{CH}_2\text{CO}_2\text{H})$.

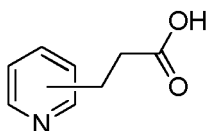
CONH₂, -CO₂Me, -CONMe₂, -CO₂Et, -CONEt₂, -CONMeEt, -C(NO₂)(NH₂), -C(NO₂)(NMe₂), -C(NO₂)(NEt₂), and -C(NO₂)(NMeEt).

Examples of compounds of formula (7a), (7b) and (7c) include but are not limited to 4-cyanopyridine, 2-cyanopyridine, nicotinic hydrazide, iso-nicotinamide, nicotinamide, iso-nicotinic acid, nicotinic acid, nicotine, methyl nicotinate, N,N-dimethylnicotinamide, trans-3-(3-pyridyl)acrylic acid, trans-3-(4-pyridyl)acrylic acid, pyridine-3-sulfonic acid, 4-(2-pyridylazo)resorcinol, iso-nicotinaldehyde, nicotinaldehyde, bipyridyl (2,2'- and 4,4'-), quinoline, isoquinoline or other compound of formula (7a), (7b) or (7c) illustrated below.

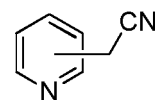




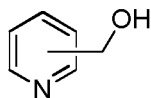
C-2: 2-Pyridylacetic acid
C-3: 3-Pyridylacetic acid
C-4: 4-Pyridylacetic acid



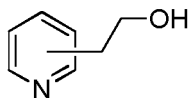
C-2: 2-Pyridylpropionic acid
C-3: 3-Pyridylpropionic acid
C-4: 4-Pyridylpropionic acid



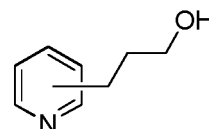
C-2: 2-Pyridylacetonitrile
C-3: 3-Pyridylacetonitrile
C-4: 4-Pyridylacetonitrile



C-2: 2-Pyridinyl methanol
C-3: 3-Pyridinyl methanol
C-4: 4-Pyridinyl methanol

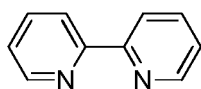


C-2: 2-Pyridinyl ethanol
C-3: 3-Pyridinyl ethanol
C-4: 4-Pyridinyl ethanol

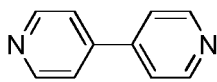


C-2: 2-Pyridinyl propanol
C-3: 3-Pyridinyl propanol
C-4: 4-Pyridinyl propanol

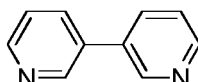
5



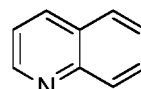
2,2'-Bipyridyl



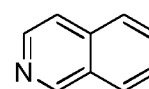
4,4'-Bipyridyl



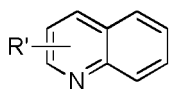
3,3'-Bipyridyl



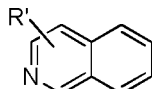
Quinoline



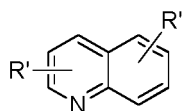
Isoquinoline



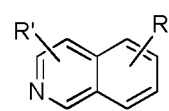
R' @ C-2, C-3 or C-4;
R' = Me, Et, CN, CO₂H,
CO₂Me or CO₂Et



R' @ C-2, C-3 or C-4;
R' = Me, Et, CN, CO₂H,
CO₂Me or CO₂Et



R' @ C-2, C-3 or C-4;
R' = Me, Et, CN, CO₂H,
CO₂Me or CO₂Et



R' @ C-2, C-3 or C-4;
R' = Me, Et, CN, CO₂H,
CO₂Me or CO₂Et

R'' @ C-5, C-6, C-7 or C-8;
R'' = Me, Et, CN, CO₂H,
CO₂Me or CO₂Et

R'' @ C-5, C-6, C-7 or C-8;
R'' = Me, Et, CN, CO₂H,
CO₂Me or CO₂Et

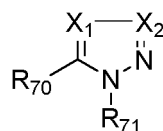
It is possible for a compound of formula (7) to convert to another compound of formula (7) under the conditions used in the plating bath of the present invention, i.e. such as one compound of formula (7a) to another compound of formula (7a), a compound (7b) to another compound (7b) or a compound (7c) to another compound (7c). For example, 4-cyanopyridine, iso-nicotinamide and iso-nicotinaldehyde may each convert to iso-nicotinic acid, whereas 3-cyanopyridine, nicotinamide, nicotinaldehyde and nicotinic hydrazide may each convert to nicotinic acid. The compound of formula (7) therefore includes within its scope the starting compound of formula (7), the converted compound of formula (7) and mixtures thereof. In this embodiment, it is not envisaged that e.g. a compound (7a) would convert to e.g. a compound (7c) or vice versa.

When the compound of formula (7a), (7b) or (7c) is an addition salt, the salt may be an alkali metal salt, an alkaline earth metal salt or an ammonium salt. In one preferred embodiment, the salt is a

sodium, potassium, calcium or ammonium salt. Examples of salts of compound of formula (7a), (7b) or (7c) include but are not limited to nicotinic acid sodium salt, nicotinic acid potassium salt, nicotinic acid calcium salt, nicotinic acid ammonium salt, iso-nicotinic acid sodium salt, iso-nicotinic acid potassium salt, iso-nicotinic acid calcium salt and iso-nicotinic acid ammonium salt.

5

When the leveller is a substituted or unsubstituted triazole, the triazole may be a 1,2,3- or a 1,2,4-triazole. In one embodiment, the leveller is a compound of formula (8):



(8)

10

wherein R_{70} is selected from a group consisting of H, $-CO_2R_{72}$ and $-NR_{72}R_{73}$;

R_{71} is selected from a group consisting of H and unsubstituted C_1 - C_{10} -alkyl;

R_{72} and R_{73} are independently selected from the group consisting of H and unsubstituted C_1 - C_{10} -alkyl; one of X_1 and X_2 is C- R_{74} and the other of X_1 and X_2 is N; and

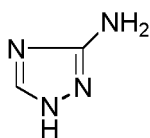
15

R_{74} is selected from a group as defined for R_{70} .

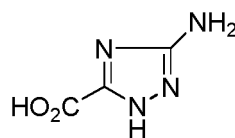
In one embodiment, X_1 is C- R_{74} and X_2 is N. In another embodiment, X_2 is C- R_{74} and X_1 is N.

Preferably, R_{70} is selected from a group consisting of H, $-CO_2H$, $-CO_2Me$, $-CO_2Et$, $-CO_2Pr$ (n- or i-), $-CO_2Bu$ (n-, i- or t-), $-NH_2$, $-NHMe$, $-NHET$, $-NHPr$ (n- or i-), $-NHBu$ (n-, i- or t-), $-NMe_2$, $-NEt_2$, $-NPr_2$ (wherein each Pr group is independently n- or i-) and $-NBu_2$ (wherein each Bu group is independently n-, i- or t-). R_{72} and R_{73} therefore are independently selected from the group consisting of H, methyl, ethyl, propyl (n-or i-) and butyl (n-, i- or t-). R_{71} is preferably selected from a group consisting of H, methyl, ethyl, propyl (n-or i-) and butyl (n-, i- or t-). R_{74} is preferably selected from the group consisting of H, $-CO_2H$, $-CO_2Me$, $-CO_2Et$, $-CO_2Pr$ (n- or i-), $-CO_2Bu$ (n-, i- or t-), $-NH_2$, $-NHMe$, $-NHET$, $-NHPr$ (n- or i-), $-NHBu$ (n-, i- or t-), $-NMe_2$, $-NEt_2$, $-NPr_2$ (wherein each Pr group is independently n- or i-) and $-NBu_2$ (wherein each Bu group is independently n-, i- or t-). Examples of compounds of formula (8) include but are not limited to 3-amino-1,2,4-triazole and 3-amino-1,2,4-triazole-5-carboxylic acid.

30

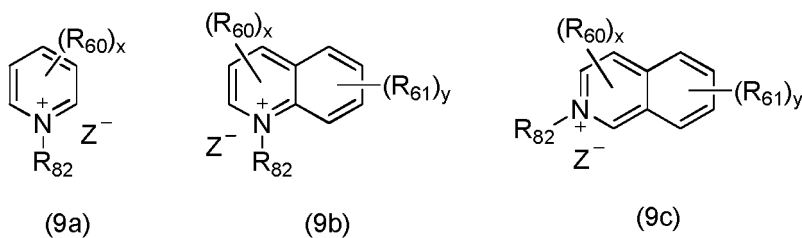


3-Amino-1,2,4-triazole



3-Amino-1,2,4-triazole-5-carboxylic acid

The leveller may be a substituted or unsubstituted pyridinium salt. Preferably, the leveller is a compound of formula (9a), (9b) or (9c):



5

wherein R_{60} and R_{61} are independently selected from the group consisting of $-OH$, $-CN$, $-CONR_{62}R_{63}$, $-CO_2R_{62}$, $-COR_{63}$, N -(unsubstituted C_1 - C_{10} -alkyl)-pyrrolidinyl, unsubstituted C_1 - C_{10} -alkyl, substituted C_1 - C_{10} -alkyl, unsubstituted C_2 - C_{10} -alkenyl, substituted C_2 - C_{10} -alkenyl, $-SO_2-R_{63}$, $-N=N$ -(unsubstituted C_6 - C_{10} -aryl), $-N=N$ -(substituted C_6 - C_{20} -aryl), unsubstituted pyridyl, substituted pyridyl,

10 wherein the substituents are independently selected from the group consisting of at least one (e.g. 1, 2, 3, 4 or 5) of $-CN$, $-CONR_{64}R_{65}$, $-COR_{65}$, $-CO_2R_{64}$, $-OH$, $-NR_{64}R_{65}$ and $=NR_{64}$;

R_{62} is selected from the group consisting of H , $-OH$ and unsubstituted C_1 - C_{10} -alkyl;

R_{63} is selected from the group consisting of H , $-OH$, unsubstituted C_1 - C_{10} -alkyl, unsubstituted C_1 - C_{10} -alkyl- CO_2H , $-NH_2$, $-NH$ (unsubstituted C_1 - C_{10} -alkyl), $-N$ (unsubstituted C_1 - C_{10} -alkyl) $_2$;

15 R_{64} is selected from the groups defined for R_{62} ;

R_{65} is selected from the groups defined for R_{63} ;

R_{82} is selected from the group consisting of $-O^-$ and unsubstituted C_1 - C_{10} -alkyl;

Z is a counterion when R_{82} is an unsubstituted C_1 - C_{10} -alkyl;

each x is 0, 1, 2 or 3; and

20 each y is 0, 1, 2, 3 or 4.

In one embodiment, the leveller is a compound of formula (9a). In another embodiment, the leveller is a compound of formula (9b). In yet another embodiment, the leveller is a compound of formula (9c).

25 The various embodiments for R_{60} , R_{61} , R_{62} , R_{63} , R_{64} , R_{65} , x and y are as generally described above with regard to the compounds of formulae (7a), (7b) and (7c) and each of these embodiments can be considered recited herein with regard to the compounds of formulae (9a), (9b) and (9c).

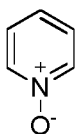
R_{82} is a substituent attached to the nitrogen atom. In one embodiment, R_{82} may be $-O^-$ i.e. the compound of formula (9a), (9b) or (9c) is an N-oxide. In this instance, a counterion Z is generally not required in order to stabilise the pyridinyl N atom. In another embodiment, R_{82} may be an unsubstituted C_1 - C_{10} -alkyl, such as methyl, ethyl, propyl (n-or i-), butyl (n-, i- or t-). In this embodiment, a counterion Z is required and any suitable counterion may be utilised, for example, halide anions such as F^- , Cl^- , Br^- or I^- .

35

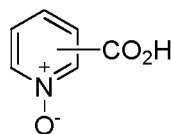
It is possible for a compound of formula (9) to convert to another compound of formula (9) under the conditions used in the plating bath of the present invention, i.e such as one compound of formula (9a) to another compound of formula (9a), a compound (9b) to another compound (9b) or a compound (9c) to another compound (9c). The compound of formula (9) therefore includes within its scope the starting compound of formula (9), the converted compound of formula (9) and mixtures thereof. In this embodiment, it is not envisaged that e.g. a compound (9a) would convert to e.g. a compound (9c) or vice versa.

Examples of compounds of formula (9a), (9b) and (9c) include but are not limited to those illustrated below:

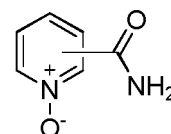
Note: Hal⁻ = halide = F⁻, Cl⁻, Br⁻ or I⁻



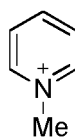
Pyridine N-oxide



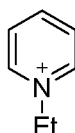
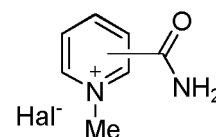
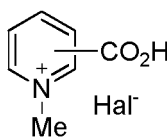
C-2: Picolinic acid N-oxide
C-3: Nicotinic acid N-oxide
C-4: Isonicotinic acid N-oxide



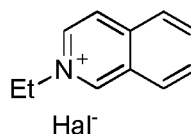
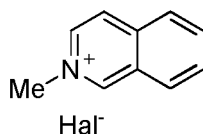
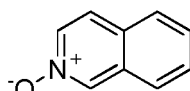
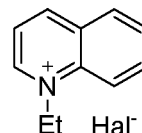
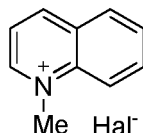
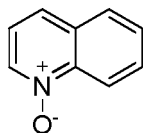
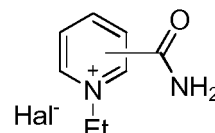
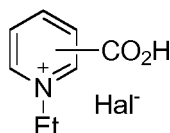
C-2: Picolinamide N-oxide
C-3: Nicotinamide N-oxide
C-4: Isonicotinamide N-oxide



N-methyl pyridinium halide



N-ethyl pyridinium halide



Alternatively, the leveller may be a substituted or unsubstituted polyalkyleneimine. In this instance, the leveller is preferably unsubstituted polyethyleneimine or ethoxylated polyethyleneimine.

Before the bath is utilised in a plating process, the leveller may be insoluble, partially soluble or substantially completely soluble in the other bath components. However, when the bath is in use it is desirable that the leveller is substantially completely soluble at the desired plating temperature.

The leveller may be added in any suitable concentration, for example, from about 0.0001 g/litre to about 10 g/litre. In one embodiment, the concentration of leveller is about ≥ 0.001 g/litre, in another embodiment about ≥ 0.01 g/litre, in another embodiment about ≥ 0.1 g/litre. In another embodiment, the concentration of leveller is about ≤ 9 g/litre, in another embodiment about ≤ 8 g/litre, in another embodiment about ≤ 7 g/litre, in another embodiment about ≤ 6 g/litre, in another embodiment about ≤ 5 g/litre. In yet another embodiment, the concentration of the leveller is about 0.01 g/litre to about 5 g/litre.

In one embodiment, the aqueous platinum electroplating bath may comprise more than one leveller e.g. 2, 3, 4, or 5 levellers. In this instance, each leveller may be independently selected from those as described above.

If desired, the plating bath of the present invention may comprise one or more other plating salts or complexes, such as platinum group metal (PGM) plating salts or complexes, or base metal plating salts or complexes. The PGM salts or complexes may be rhodium, palladium, iridium, ruthenium or rhenium plating salts or complexes, such as HReO_4 . Base metal plating salts include but are not limited to hexaamminenickel(II) chloride.

The bath may be prepared by adding the components in any suitable order, for example, in one method an acid (if used) may be added to an aqueous solution of the platinum ions, followed by the borate ion source, base (if used), leveller (if used) and other components (if used). In another method, a base may be added to an aqueous solution of a platinum borate salt, followed by a leveller (if used) and other components (if used).

Depending on the substrate to be plated, the plating baths may further comprise one or more brighteners or other components, for example, surfactants or wetting agents to suppress bubble formation on the substrate. Suitable wetting agents/surfactants include polyethyleneglycol 50% aqueous solution or long chain alkyl sarcosines.

In another aspect, the invention includes a method of plating a PGM onto a substrate, comprising electroplating using the bath of the invention. The substrate is preferably a conductive substrate, such as a metal, conductive plastic or conductive ceramic.

In another aspect, the invention includes the use of an aqueous platinum plating bath as defined herein for plating platinum or platinum alloy onto a substrate. In one embodiment, platinum is plated onto a substrate. In another embodiment, a platinum alloy is plated onto a substrate. The substrate may be a metal (e.g. a metal article or metal powder), conductive plastic or conductive ceramic (such as a zirconia oxygen sensor or ceramic ozone destructor for motor vehicles or aircraft).

The invention will now be described by way of the following non-limiting Examples and with reference to the following Figures in which:

Figure 1 illustrates a shaped part of the given dimensions which is used to assess the deposition of platinum (or platinum alloys) onto shaped parts.

Examples

General

20Q "Q salt[®]" material is commercially available from Johnson Matthey and is an ammoniacal solution of tetraammineplatinum(II) hydrogen phosphate at a pH of about 10 to 11 and 20 g/l Pt.

Unless otherwise stated, substrates were 9 x 2.5 cm panels, thickness 1 mm for 316 stainless steel and 2 mm for brass. The brass panels were either manually polished using "Brasso[®]" or grit blasted using Type 150 and 180/220 brown aerospace grade grit; stainless steel panels were cleaned and degreased using 1M sodium hydroxide solution, followed by a dip in 6M hydrochloric acid. The panels were immersed in the plating baths to a depth of 5 cm, within 150, 400 or 600 ml glass beakers.

The shaped substrates as shown in Figure 1 were of Inconel or 316 stainless steel and were treated before use by grit blasting with 180/220 brown aerospace grit and alkali cleaning using 1M sodium hydroxide solution for 6 minutes at a temperature of at least 60°C, followed by a dip (1-2 minutes) in 6M hydrochloric acid at room temperature. The substrates were washed thoroughly between each treatment.

Unless otherwise stated, each bath comprised approx. 300ml of plating solution was heated to 90°C in a 400 ml beaker containing a circular platinised titanium anode around its inner wall. The baths were subjected to magnetic stirring. pH was measured using universal indicator paper. The 30V-2A power packs were used and obtained from Thurlby.

Example 1

An aqueous platinum plating bath was prepared from 125 ml of 20Q solution (20 g/l Pt metal), 175 ml of water and 2 g of boric acid.

The bath was used to plate a shaped part using the plating conditions of 2.10v, 066ma, 90°C, pH 8, to give 0.1836 g of bright silvery platinum in 60 mins. Two further layers were successively plated on the same substrate.

- 5 Plating was continued for the second layer using the same plating conditions for a further hour to give 0.1768 g of bright silvery platinum. After the third hour, 0.1471 g of bright silvery platinum plated.

The bath was aged for 3 days at room temperature whereupon concentrated ammonia solution (0.3 ml) was added to the bath to restore the pH to 8. A shaped part was plated using plating conditions of 1.61v, 063ma, 90°C, pH8 to give 0.1460g of bright silvery platinum in 60 mins. Plating was continued using the same plating conditions for a second hour to give 0.2619 g of bright silvery platinum.

3g of boric acid was added to the bath to alter the bath's pH to 7.5 at 90°C. Using plating conditions of 1.61v, 063ma, 90°C, pH7.5, 0.1601g of bright silvery platinum was deposited in 60 mins on a shaped part.

The plating conditions were altered to 1.74v, 045ma, 90°C, pH 7.5 and 0.1305g of bright silvery platinum was deposited on a shaped part in 60 mins.

20 **Example 2**

An aqueous platinum plating bath was prepared from 5g platinum tetraamine hydrogen carbonate, 8g boric acid and 300 ml water.

The bath was used to plate a shaped part using plating conditions of 1.6v, 075ma, 90°C, pH 8, to give 0.2113 g of bright silvery platinum in 60 mins.

When the boric acid was increased to 14g (pH 7.5-8), a shaped part was plated with 0.2629 g of bright platinum.

30 The bath was aged for 174 days at room temperature before being used to plate a polished brass plaque (approx. 20 cm²) at 2.3v, 065ma, pH 7.5-8, 90°C to give 0.1900g of bright reflective platinum in 60 mins and 0.3795g in 120 mins.

The bath was heat aged in an oven for 62 days at 90°C and was then used to plate a shaped part at 1.54v, 064ma, 90°C, pH 8, to give 0.1435g of bright platinum in 60 mins.

Using the plating conditions as detailed in the following table, three shaped test parts (see Figure 1) were successively plated.

Part no.	Plating conditions	Quantity of Pt plated / g	Comments
1	2.23v, 80-100ma, pH of bath = 8, temperature of bath = 90°C, plating time = 90 mins	0.1117 g	Grey matt appearance
2	1.86v, 046ma, pH of bath = 8, temperature of bath = 90°C, plating time = 90 mins	0.1420 g	Bright silvery appearance
3	0.77v, 051ma, pH of bath = 8, temperature of bath = 90°C, plating time = 59 mins	0.1053 g	Bright silvery appearance

Example 3

An aqueous platinum plating bath was prepared from 33g of platinum tetraamine hydroxide solution (9.4% Pt w/w), 300ml water and 9g boric acid.

5

Using the plating conditions as detailed in the following table, two polished brass plaques were successively plated.

Part no.	Plating conditions	Quantity of Pt plated / g	Comments
1	1.9v, 065ma, pH of bath = 8-8.5, temperature of bath = 90°C, plating time = 30 mins then 1.75v, 080ma, pH of bath = 8-8.5, temperature of bath = 90°C, plating time = 60 mins	0.1783 g	Bright silvery appearance
2	1.75v, 080ma, pH of bath = 8, temperature of bath = 90°C, plating time = 60 mins	0.2417g	Bright silvery appearance

10

Example 4

An aqueous platinum plating bath was prepared from 125 ml 20Q solution (20g/l Pt), 175ml water and 4.95g boric acid.

Using plating conditions of 1.7v, 063 ma, pH 7.5-8, 90°C for 30 mins then 1.89v, 080ma, 90°C, for 60 mins, gave 0.2838g of bright silvery platinum on a shaped part.

5 **Example 5**

An aqueous platinum plating bath was prepared from 120ml 20Q solution (20g/l Pt as metal), 180ml water, 2g of boric acid (to neutralise the solution to pH 8), 5.7g sodium tetraborate decahydrate (pH now 10 at room temperature), followed by a further 1.5g boric acid to take the pH down to 8.5.

- 10 Using the plating conditions as detailed in the following table, four shaped parts were successively plated.

Part no.	Plating conditions	Quantity of Pt plated / g	Comments
1	0.24v, 070ma, pH of bath = 8.5-9 during plate, temperature of bath = 90°C, plating time = 90 mins	0.2208 g	Bright silvery appearance
2	0.88v, 129ma, pH of bath = 8.5-9, temperature of bath = 90°C, plating time = 60 mins	0.2414g	Bright silvery appearance
3	0.73v, 061ma, pH of bath = 8.5, temperature of bath = 90°C, plating time = 90 mins	0.1318 g	Bright silvery appearance
4	0.92v, 100ma, pH of bath = 8.5, temperature of bath = 90°C, plating time = 62 mins	0.2363g	Bright silvery appearance

Example 6

- 15 An aqueous platinum plating bath was prepared from 125 ml 20Q solution (20g/l Pt), 175ml water, 2g boric acid and 1g of sodium tetraborate decahydrate.

Using plating conditions of 2.02v, 069 ma, pH 8.5-9, 90°C for 60 mins gave 0.1908g of bright silvery platinum on a shaped part.

20

The boric acid content was increased to 5g. Using plating conditions of 1.91v, 070ma, pH 7.5-8, 90°C for 60 mins deposited 0.1878g of bright silvery platinum on a shaped part.

Example 7

An aqueous platinum plating bath was prepared from 120 ml P-salt solution (25g/l Pt), 180ml water, 2.5g boric acid and 1.5g of sodium tetraborate decahydrate.

- 5 Using plating conditions of 1.04v, 101ma, pH 8.5-9, 90°C for 110 mins gave 0.1610g of bright silvery platinum on a shaped part.

Example 8

- 10 An aqueous platinum plating bath was prepared from 125ml 20Q solution (20g/l Pt as metal), 175ml water, 4g of boric acid and 2g ammonium baborate tetrahydrate $[(\text{NH}_4)_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}]$.

Using the plating conditions as detailed in the following table, three shaped parts were successively plated.

Part no.	Plating conditions	Quantity of Pt plated / g	Comments
1	0.34v, 062ma, pH of bath = 8.5, temperature of bath = 90°C, plating time = 67 mins	0.1811 g	Bright silvery appearance
2	0.95v, 076ma, pH of bath = 8.5, temperature of bath = 90°C, plating time = 120 mins	0.1948g	Bright silvery appearance
3	0.95v, 076ma, pH of bath = 8.5, temperature of bath = 100°C, plating time = 60 mins	0.2087 g	Bright silvery appearance

15

Example 9

An aqueous platinum plating bath was prepared from 120ml P-salt solution (25g/l Pt as metal), 180ml water, 4.5g of boric acid and 1.5g sodium metaborate.

- 20 Using the plating conditions as detailed in the following table, two shaped parts were successively plated.

Part no.	Plating conditions	Quantity of Pt plated / g	Comments
1	1.79v, 108ma, pH of bath = 10, temperature of bath = 90°C, plating time = 60 mins	0.1775 g	Bright silk appearance

2*	1.92v, 121ma, pH of bath = 10, temperature of bath = 90°C, plating time = 120 mins	0.3365g	Bright silk appearance
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* The bath was aged for 5 days at room temperature before plating the second part.

Example 10

An aqueous platinum plating bath was prepared from 120ml P-salt solution (25g/l Pt as metal), 180ml water, 8g of boric acid and 1g lithium metaborate.

Using the plating conditions as detailed in the following table, three shaped parts were successively plated.

Part no.	Plating conditions	Quantity of Pt plated / g	Comments
1	1.76v, 076ma, pH of bath = 8.5, temperature of bath = 90°C, plating time = 90 mins	0.0924 g	Bright silvery appearance
2	2.08v, 108ma, pH of bath = 8.5, temperature of bath = 90°C, plating time = 100 mins	0.2254 g	Bright silvery appearance
3	1.64v, 060ma, pH of bath = 8.5, temperature of bath = 90°C, plating time = 100 mins	0.0721 g	Bright silvery appearance

Example 11

An aqueous platinum plating bath was prepared from 125ml 20Q solution (20g/l Pt as metal), 175ml water, 2.5g of boric acid, 1.5g lithium metaborate and 0.042g nicotinic acid.

Using the plating conditions as detailed in the following table, three shaped parts were successively plated.

Part no.	Plating conditions	Quantity of Pt plated / g	Comments
1	0.89v, 052ma, pH of bath = 8.5-9, temperature of bath = 95°C, plating time = 100 mins	0.2246 g	Light grey matt appearance
2	0.99v, 070ma,	0.1968 g	Dark grey matt

	pH of bath = 8.5-9, temperature of bath = 90°C, plating time = 100 mins		appearance
3	0.96v, 051ma, pH of bath = 8.5-9, temperature of bath = 90°C, plating time = 100 mins	0.1993 g	Grey matt appearance

Example 12

An aqueous platinum plating bath was prepared from 120ml P-salt solution (25g/l Pt as metal), 180ml water, 8g of boric acid, 1g lithium metaborate and 0.042g nicotinic acid.

5

Using the plating conditions as detailed in the following table, a single shaped part was successively plated.

Part no.	Plating conditions	Quantity of Pt plated / g	Comments
1	1.85v, 075ma, pH of bath = 8.5, temperature of bath = 90°C, plating time = 140 mins	0.0820 g in 140 mins	Light grey silk appearance
	1.85v, 075ma, pH of bath = 8.5, temperature of bath = 90°C, plating time = 60 mins	0.0933g in 60 mins	Bright silk appearance
		Cumulative quantity of Pt plated = 0.0820g + 0.0933g = 0.1753g in 200 mins	

10 **Example 13**

An aqueous platinum plating bath was prepared from 120ml 20Q solution (20g/l Pt metal), 180ml of water, 1ml of 40% phosphoric acid and 1g of sodium metaborate hydrate. A shaped part (see Figure 1) was plating using the conditions of 1.97V, 071ma, 90°C, pH 8 to give 0.24288g of bright white silvery platinum in 90 mins.

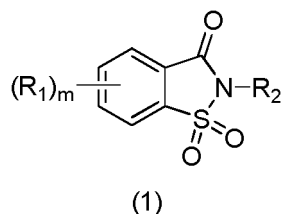
15

A further 0.5g of sodium metaborate hydrate was added to the bath, along with 1.5ml of conc. ammonia. A shaped part was plated using the conditions of 2.02v, 070ma, 90°C, pH 9 to give 0.1535g of bright white silvery platinum in 90 mins.

Claims

1. An aqueous platinum electroplating bath comprising:
 - a) a source of platinum ions; and
 - b) a source of borate ions.
2. A bath according to claim 1, wherein the source of platinum ions is at least one platinum plating salt or complex.
3. A bath according to claim 2, wherein the platinum plating salt or complex is selected from the group consisting of diammine dinitroplatinum(II), tetraammineplatinum(II) hydrogen orthophosphate, tetraammineplatinum(II) hydrogen carbonate, tetraammineplatinum(II) hydroxide, tetraammineplatinum(II) sulphate and tetraammineplatinum(II) nitrate.
4. A bath according to claim 2, wherein the platinum plating salt or complex is selected from the group consisting of alkali metal hexahydroxyplatinate(IV), alkali metal tetranitroplatinate(II), alkali metal salts of hydrogen hexachloroplatinate(IV), alkali metal salts of hydrogen dinitrosulphatoplatinate(II), tetraammineplatinum(II) halides and alkali metal tetrahaloplatinate(II).
5. A bath according to any one of the preceding claims, wherein the source of borate ions is boron-containing acid optionally in combination with at least one borate salt.
6. A bath according to claim 5, wherein the boron-containing acid is selected from the group consisting of boric acid, tetraboric acid and pyroboric acid.
7. A bath according to any one of claims 1 to 4, wherein the source of borate ions is a metaborate salt optionally in combination with at least one other borate salt.
8. A bath according to claim 5 or claim 7, wherein the borate salt is selected from the group consisting of alkali metal metaborates, alkali metal tetraborates, alkali metal diborates, alkali metal pentaborates, alkaline earth metal metaborates, alkaline earth metal tetraborates, alkaline earth metal diborates and alkaline earth metal pentaborates.
9. A bath according to claim 1, wherein the source of platinum ions and the source of borate ions is a platinum borate salt or complex.
10. A bath according to any one of the preceding claims, wherein the platinum ion concentration is about 0.1 to about 30 g/litre.
11. A bath according to any one of the preceding claims, wherein the borate ion concentration is about 0.1 to about 90 g/litre.

12. A bath according to any one of the preceding claims further comprising at least one leveller.
13. A bath according to claim 12, wherein the leveller comprises at least one unsaturated carbon-carbon or unsaturated carbon-heteroatom bond.
14. A bath according to claim 12 or claim 13, wherein the leveller is selected from the group consisting of at least one:
- substituted or unsubstituted saccharine or salt thereof;
 - substituted or unsubstituted benzopyranone;
 - substituted or unsubstituted benzaldehyde or derivative thereof;
 - substituted or unsubstituted alkene provided the alkene is not ethylene;
 - substituted or unsubstituted alkyne provided the alkyne is not acetylene;
 - substituted or unsubstituted alkylnitrile;
 - substituted or unsubstituted pyridine or addition salt thereof;
 - substituted or unsubstituted triazole; and
 - substituted or unsubstituted pyridinium salt.
15. A bath according to any one of the claims 12 to 14, wherein the leveller is a compound of formula (1) or salts thereof:

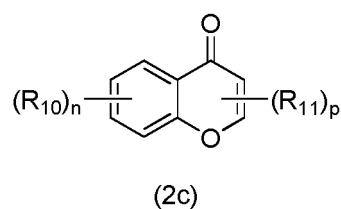
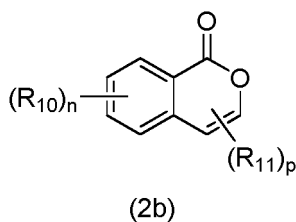
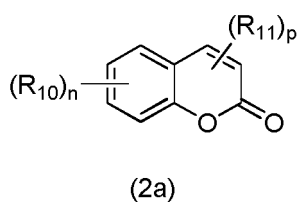


wherein m is 0, 1, 2, 3 or 4;

each R_1 is independently an unsubstituted C_1 - C_{10} alkyl group;

R_2 is selected from the group consisting of H, unsubstituted C_1 - C_{10} alkyl, an alkali metal ion and an alkaline earth metal ion.

16. A bath according to any one of the claims 12 to 14, wherein the leveller is a compound of formula (2a), (2b) or (2c):



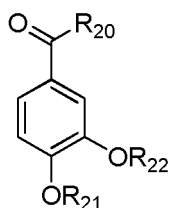
wherein n is 0, 1, 2, 3 or 4;

p is 0, 1 or 2;

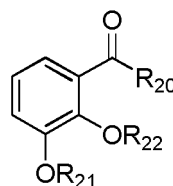
each R₁₀ and R₁₁ is independently selected from an unsubstituted C₁-C₁₀ alkyl group.

5

17. A bath according to any one of the claims 12 to 14, wherein the leveller is a compound of formula (3a) or (3b):



(3a)



(3b)

10

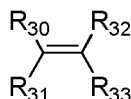
wherein R₂₀ is selected from the group consisting of H and -OR₂₃; and

R₂₁ and R₂₂ are independently selected from the group consisting of H, -C(O)R₂₄ and unsubstituted C₁-C₁₀-alkyl; and

R₂₃ and R₂₄ are independently selected from the group consisting of H and unsubstituted C₁-C₁₀-alkyl.

15

18. A bath according to any one of the claims 12 to 14, wherein the leveller is a compound of formula (4):



(4)

20

wherein each R₃₀, R₃₁, R₃₂ and R₃₃ is independently selected from the group consisting of H, unsubstituted C₁-C₁₀-alkyl, substituted C₁-C₁₀-alkyl, -CO₂R₃₄, -NR₃₄R₃₅, -CONR₃₄R₃₅ and -CN, provided that R₃₀, R₃₁, R₃₂ and R₃₃ are not all H,

25

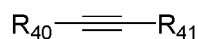
wherein the substituents are selected from the group consisting of at least one -OH, -CO₂R₃₆, -OC(O)R₃₆, -NR₃₆R₃₇, -CONR₃₆R₃₇, -CN, -SO₃⁻Na⁺ and -SO₃⁻K⁺;

R₃₄ and R₃₅ are independently selected from the group consisting of H and unsubstituted C₁-C₁₀-alkyl; and

R₃₆ and R₃₇ are independently selected from the group consisting of H and unsubstituted C₁-C₁₀-alkyl.

30

19. A bath according to any one of the claims 12 to 14, wherein the leveller is a compound of formula (5):



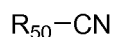
(5)

wherein R_{40} and R_{41} are independently selected from the group consisting of H, unsubstituted C_1 - C_{10} -alkyl and substituted C_1 - C_{10} -alkyl, provided that R_{40} and R_{41} are not both H,

wherein the substituents are selected from the group consisting of at least one of -OH, $-\text{CO}_2R_{42}$, $-\text{OC(O)}R_{42}$, $-\text{NR}_{42}R_{43}$, $-\text{CONR}_{42}R_{43}$, -CN, $-\text{SO}_3^-\text{Na}^+$ and $-\text{SO}_3^-\text{K}^+$;

R_{42} and R_{43} are independently selected from the group consisting of H and unsubstituted C_1 - C_{10} -alkyl.

20. A bath according to any one of the claims 12 to 14, wherein the leveller is a compound of formula (6):

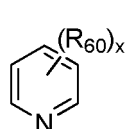


(6)

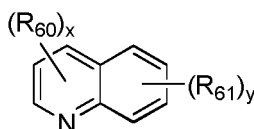
wherein R_{50} is a substituted or unsubstituted C_1 - C_{10} -alkyl, and the substituents are selected from the group consisting of at least one of $-\text{OR}_{51}$, $-\text{CO}_2R_{51}$, $-\text{OC(O)}R_{51}$, $-\text{NR}_{51}R_{52}$ and -CN; and

wherein R_{51} and R_{52} are independently selected from the group consisting of H and unsubstituted C_1 - C_{10} -alkyl.

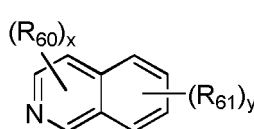
21. A bath according to any one of the claims 12 to 14, wherein the leveller is a compound of formula (7a), (7b) or (7c):



(7a)



(7b)



(7c)

wherein R_{60} and R_{61} are independently selected from the group consisting of -OH, -CN, $-\text{CONR}_{62}R_{63}$, $-\text{CO}_2R_{62}$, $-\text{COR}_{63}$, *N*-(unsubstituted C_1 - C_{10} -alkyl)-pyrrolidinyl, unsubstituted C_1 - C_{10} -alkyl, substituted C_1 - C_{10} -alkyl, unsubstituted C_2 - C_{10} -alkenyl, substituted C_2 - C_{10} -alkenyl, $-\text{SO}_2R_{63}$, $-\text{N}=\text{N}$ -(unsubstituted C_6 - C_{10} -aryl), $-\text{N}=\text{N}$ -(substituted C_6 - C_{20} -aryl), unsubstituted pyridyl, substituted pyridyl,

wherein the substituents are independently selected from the group consisting of at least one of $-\text{CN}$, $-\text{CONR}_{64}\text{R}_{65}$, $-\text{COR}_{65}$, $-\text{CO}_2\text{R}_{64}$, $-\text{OH}$, $-\text{NR}_{64}\text{R}_{65}$ and $=\text{NR}_{64}$;

R_{62} is selected from the group consisting of H , $-\text{OH}$ and unsubstituted $\text{C}_1\text{-C}_{10}\text{-alkyl}$;

R_{63} is selected from the group consisting of H , $-\text{OH}$, unsubstituted $\text{C}_1\text{-C}_{10}\text{-alkyl}$, unsubstituted $\text{C}_1\text{-C}_{10}\text{-alkyl-CO}_2\text{H}$, $-\text{NH}_2$, $-\text{NH}(\text{unsubstituted } \text{C}_1\text{-C}_{10}\text{-alkyl})$, $-\text{N}(\text{unsubstituted } \text{C}_1\text{-C}_{10}\text{-alkyl})_2$;

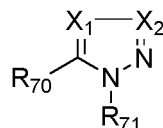
R_{64} is selected from the groups defined for R_{62} ;

R_{65} is selected from the groups defined for R_{63} ;

each x is 0, 1, 2 or 3; and

each y is 0, 1, 2, 3 or 4.

22. A bath according to any one of the claims 12 to 14, wherein the leveller is a compound of formula (8):



(8)

wherein R_{70} is selected from a group consisting of H , $-\text{CO}_2\text{R}_{72}$ and $-\text{NR}_{72}\text{R}_{73}$;

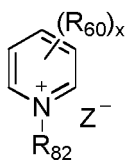
R_{71} is selected from a group consisting of H and unsubstituted $\text{C}_1\text{-C}_{10}\text{-alkyl}$;

R_{72} and R_{73} are independently selected from the group consisting of H and unsubstituted $\text{C}_1\text{-C}_{10}\text{-alkyl}$;

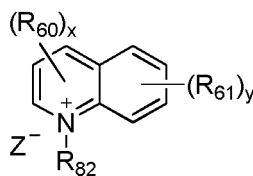
one of X_1 and X_2 is C-R_{74} and the other of X_1 and X_2 is N ; and

R_{74} is selected from a group as defined for R_{70} .

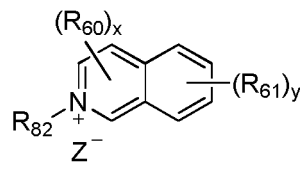
23. A bath according to any one of the claims 12 to 14, wherein the leveller is a compound of formula (9a), (9b) or (9c):



(9a)



(9b)



(9c)

wherein R_{60} and R_{61} are independently selected from the group consisting of $-\text{OH}$, $-\text{CN}$, $-\text{CONR}_{62}\text{R}_{63}$, $-\text{CO}_2\text{R}_{62}$, $-\text{COR}_{63}$, $\text{N}(\text{unsubstituted } \text{C}_1\text{-C}_{10}\text{-alkyl})\text{-pyrrolidinyl}$, unsubstituted $\text{C}_1\text{-C}_{10}\text{-alkyl}$, substituted $\text{C}_1\text{-C}_{10}\text{-alkyl}$, unsubstituted $\text{C}_2\text{-C}_{10}\text{-alkenyl}$, substituted $\text{C}_2\text{-C}_{10}\text{-alkenyl}$, $-\text{SO}_2\text{-R}_{63}$, $-\text{N}=\text{N}(\text{unsubstituted } \text{C}_6\text{-C}_{10}\text{-aryl})$, $-\text{N}=\text{N}(\text{substituted } \text{C}_6\text{-C}_{20}\text{-aryl})$, unsubstituted pyridyl, substituted pyridyl,

wherein the substituents are independently selected from the group consisting of at least one – CN, –CONR₆₄R₆₅, –COR₆₅, –CO₂R₆₄, –OH, –NR₆₄R₆₅ and =NR₆₄;

R₆₂ is selected from the group consisting of H, –OH and unsubstituted C₁–C₁₀-alkyl;

R₆₃ is selected from the group consisting of H, –OH, unsubstituted C₁–C₁₀-alkyl, unsubstituted C₁–C₁₀-alkyl-CO₂H, –NH₂, –NH(unsubstituted C₁–C₁₀-alkyl), –N(unsubstituted C₁–C₁₀-alkyl)₂;

R₆₄ is selected from the groups defined for R₆₂;

R₆₅ is selected from the groups defined for R₆₃;

R₈₂ is selected from the group consisting of –O[–] and unsubstituted C₁–C₁₀-alkyl;

Z is a counterion when R₈₂ is an unsubstituted C₁–C₁₀-alkyl;

each x is 0, 1, 2 or 3; and

each y is 0, 1, 2, 3 or 4.

24. A bath according to claim 12, wherein the leveller is at least one substituted or unsubstituted polyalkyleneimines.

25. A bath according to any one of the preceding claims, further comprising one or more other platinum group metal or base metal plating salts or complexes.

26. A bath according to any one of the preceding claims, wherein the rate of plating is about ≥0.5 microns thickness of platinum or platinum alloy per hour.

27. A bath according to any one of the preceding claims, wherein the pH when the bath is ready for use or in use is in the range of about 2 to about 14.

28. A bath according to any one of the preceding claims, wherein the bath is used at temperatures from about room temperature to about 100°C.

29. A bath according to any one of the preceding claims further comprising one or more brighteners, surfactants or wetting agents.

30. The use of an aqueous platinum electroplating bath according to any one of claims 1 to 29 for plating platinum or a platinum alloy onto a substrate.