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(54) **ZINC-NICKEL ELECTROPLATING**
ZINK-NICKEL-ELEKTROPLATTIERUNG
ELECTRODEPOSITION ZINC-NICKEL

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Description

Technical Field

[0001] The present invention relates to an apparatus and process for zinc-nickel electroplating.

Description of the Prior Art

[0002] US 5,162,079 A discloses an apparatus for electroplating metals. The apparatus comprises an electroplating bath which contains a plating solution of a metallic salt, for instance, nickel sulfate. A cathode workpiece is positioned in the bath. An insoluble anode assembly is also provided in the bath. The anode assembly includes an anode which is essentially insoluble during electroplating and an anion exchange membrane enclosure around the anode. An electrically conductive acid solution is contained within the enclosure of the anode assembly.

[0003] The flow of current in the apparatus causes anions, for instance sulfate ions, in the plating solution to travel through the anion exchange membrane increasing the acid concentration within the anode assembly enclosure.

[0004] Accumulated acid is periodically flushed from the enclosure.

[0005] One purpose of the apparatus of US 5,162,079 A is to inhibit the increase in concentration of dissolved metal in the electroplating bath due to a cathode efficiency which is less than the anode efficiency.

[0006] U. S. Patent No. 4, 778,572 discloses an apparatus similar to that of US 5,162,079 A. An electroplating apparatus for plating nickel onto a workpiece is provided.

[0007] A nickel-plating bath is provided in the apparatus. The bath is a typical Watts nickel low pH acid bath. A cathode workpiece is positioned in the bath. An anode structure is also positioned in the bath. The anode structure comprises a series of nickel plate anodes. The nickel plate anodes are enclosed in an ion exchange membrane that allows a current flow from the anodes to the cathode workpiece while at the same time shielding the anodes from organics, such as Coumarin within the bath. The nickel plate anodes are immersed in dilute sulfuric acid contained within the ion exchange membrane enclosure.

[0008] DE 198 34 353 A1 discloses an apparatus similar to that of US 5,162,079 A for applying a zinc-nickel coating onto a cathode workpiece. The apparatus comprises a vessel which is divided by a cation exchange membrane into a cathode compartment containing a catholyte and an anode compartment containing an anolyte. The catholyte is an alkaline zinc-nickel electroplating bath containing poly (alkyleneimine) additives for complexing and brightening. A cathode workpiece to be plated is positioned in the cathode compartment. The anolyte is an acid such as sulfuric acid or phosphoric acid. A platinum coated titanium anode is immersed in the anolyte. The ion exchange membrane allows the flow

of current from the anode to the cathode, but at the same time shields the anode from the alkaline zinc-nickel electroplating bath.

[0009] Electrolysis of alkaline zinc-nickel baths containing poly (alkyleneimines) produces amine breakdown at the anode into nitriles and cyanides if the anode is exposed to the plating bath. The ion exchange membrane prevents such amine breakdown. However, an apparatus which comprises an alkaline electroplating bath adjacent to an acid anolyte can be dangerous. In addition, a platinum coated titanium anode is expensive.

[0010] Attention is also drawn to DE 37 12 511 A1 and WO 98/40 539 A1.

Brief Description of the Drawings

[0011] The present invention and advantages thereof will become more apparent upon consideration of the following specification with reference to the accompanying drawings in which:

Fig. 1 is a schematic illustration of a zinc-nickel electroplating apparatus in accordance with the present invention; and

Fig. 2 is a schematic illustration of an anode assembly in the apparatus of Fig. 1.

Summary of the Invention

[0012] The present invention relates to an apparatus for applying a zinc-nickel electroplate to a workpiece, as defined in claim 1. The apparatus comprises a zinc-nickel electroplating bath comprising an amine additive, such as a poly (alkyleneimines) capable of being oxidized in the bath to cyanides.

[0013] The bath has a pH more than about 14. A cathode workpiece is positioned in said bath. An anode assembly is in contact with the bath. The anode assembly comprises an enclosure defining an anolyte compartment, at least a portion of the enclosure in contact with the bath being an ion exchange membrane. An anolyte is positioned in the compartment. An insoluble metal anode is immersed in the anolyte. The anolyte is a sodium or potassium hydroxide solution comprising 50 to about 760 g/liter of sodium or potassium hydroxide. The anode is a mild steel, a steel alloy or an iron chromium alloy.

[0014] The present invention also resides in a process for applying a zinc-nickel electroplate to a workpiece as defined in claim 5 or 6. A zinc-nickel electroplating bath comprising amine additives and having a pH more than about 14 is provided. A cathode workpiece is positioned in the bath. An anode assembly is provided in the bath. The anode assembly comprises an enclosure defining an anolyte compartment, at least a portion of the enclosure in contact with the bath being an ion exchange membrane. An anolyte is positioned in the compartment. An insoluble metal anode is immersed in the anolyte. The anolyte is a sodium or potassium hydroxide solution com-

prising 50 to about 760 g/liter of sodium or potassium hydroxide, and the anode is a mild steel, a steel alloy, or an iron chromium alloy. A potential is applied between the anode and cathode establishing a current flow from the anode to the cathode through the ion exchange membrane. The ion exchange membrane shields the anode from the zinc-nickel electroplating bath preventing amine breakdown into cyanides.

[0015] Preferred embodiments of the present invention may be gathered from the dependent claims.

Description of Preferred Embodiments

[0016] Referring to the Figures, the zinc-nickel electroplating apparatus 12 of the present invention comprises a tank 14.

[0017] The tank 14 contains a zinc-nickel electroplating bath 16 and a cathode workpiece 18. The tank 14 also comprises an anode assembly 20. The anode assembly 20 comprises an enclosure 22 which defines an anolyte compartment 24.

[0018] The compartment 24 is closed by the enclosure 22 on all sides and the bottom. At least one wall 26 of the enclosure 22 is an ion exchange membrane. The anolyte compartment 24 comprises an anolyte 28. An anode 30 is immersed in the anolyte 28. The enclosure 22 shields the anode 30 from the electroplating bath 16 so that no bath 16 contacts the anode 30. The ion exchange membrane 26 faces the cathode workpiece 18. This allows current to flow from the anode 30 to the cathode workpiece 18 on the application of an electric potential to the anode 30 and the cathode workpiece 18. The current flow causes plating of the cathode workpiece 18.

[0019] It will be understood by those skilled in the art that the enclosure 22 and compartment 24 can have many configurations, for instance, a membrane bag suspended in the catholyte, or a membrane containing wall extending crosswise in the tank 14 dividing the tank 14 into a catholyte compartment or an anolyte compartment.

[0020] In the present invention, the cathode workpiece 18 is any workpiece typically used in zinc-nickel electroplating.

[0021] In the example of the Figures, a steel plate was used.

[0022] The enclosure 22 of the anode assembly 20 can be made of any suitable plastic resistant to the zinc-nickel electroplating bath 16 and the anolyte 28, for instance, polyethylene.

[0023] The ion exchange membrane 26 of the enclosure 22 can be any ion exchange membrane used in an electroplating bath, for example, an ion exchange membrane, such as a perfluorosulfonic acid ion exchange membrane, marketed by E. I. DuPont de Nemours under the trademark NAFION. In the following Examples, a NAFION 450 membrane was used.

[0024] The anolyte 28 in the anolyte compartment 24 is an alkaline solution of potassium hydroxide or sodium hydroxide. These alkaline solutions can have concentra-

tions, by way of example, in the range of one molar to about 20 molar hydroxide, with a preferred concentration range of 1 to 10 molar. A preferred anolyte is about 50 g/liter sodium hydroxide to about 760 g/liter.

[0025] The anode 30 of the anode assembly 20 is a mild steel, a steel alloy, or an iron chromium alloy such as stainless steel.

[0026] The zinc-nickel electroplating bath is an aqueous solution that is alkaline having a pH which is preferably above about 14. The bath contains an inorganic alkaline component in an effective amount to achieve this pH.

[0027] Amounts from about 50 grams per liter to about 200 grams per liter, based on the electroplating bath of the alkaline component can be used. Examples of suitable alkaline components are alkali metal derivatives such as sodium hydroxide and potassium hydroxide.

[0028] The electroplating bath 16 also contains a controlled amount of zinc ions and a controlled amount of nickel ions.

[0029] The source for the zinc ions for the electroplating bath 16 can be any zinc compound which is soluble in an alkaline aqueous medium. Examples of zinc compounds which can be added to the electroplating bath are zinc oxide or a soluble salt such as zinc sulfate, zinc carbonate, zinc sulfamate, and zinc acetate. The concentration of zinc ions in the electroplating bath is from about 1 to 100 grams per liter, preferably about 4 to about 50 grams per liter (about 4,000 to about 50,000 ppm). At a pH above about 14, the predominant zinc species in the bath is zincate ion.

[0030] The source for the nickel ions for the electroplating bath can be any nickel compound which can be made soluble in an aqueous alkaline solution. Examples of suitable nickel compounds are an inorganic or organic acid salt of nickel, such as nickel sulfate, nickel carbonate, nickel acetate, nickel sulfamate and nickel formate. The concentration of nickel ions in the electroplating bath can be from about 0.1 to about 10 grams per liter (about 100 to 10,000 ppm), more preferably in the range from about 0.1 gram per liter to about 3 grams per liter (about 100 ppm to about 3,000 ppm).

[0031] The zinc-nickel electroplating bath also contains an amine compound capable of being oxidized to cyanides in the bath, such as a polymer of an aliphatic amine.

[0032] Examples of aliphatic amine polymers oxidizable to cyanides in the bath are ethyleneimine, 1, 2-propyleneimine, 1, 2-butylenimine and 1, 1-dimethylethyleneimine. The poly (alkyleneimines) may have molecular weights from about 100 to about 100,000 and should be soluble in the bath. By way of example, poly (ethyleneimine) which is useful in the bath can have a molecular weight of from about 150 to above about 2,000. Useful poly (ethyleneimines) are available commercially, for example from BASF under the designations LUGALVAN G-15, LUGALVAN G-20 and LUGALVAN G-35. Examples of other useful poly (alkyleneimines) are tetraethyl-

enepentamine (TEPA), pentaethylenhexamine (PE-HA), and heptaethylene octamine marketed by Nippon Shokubai Co. Ltd. under the trademark EPOMIN 003.

[0033] One function of the aliphatic poly (alkylene-imines) is to complex nickel ions in the alkaline zinc-nickel bath.

[0034] It will be understood by those skilled in the art that the zinc-nickel electroplating bath may also contain other additives such as other brighteners, and metal complexing agents. One useful metal complexing agent is QUADROL from BASF. QUADROL is N, N, N', N'-tetrakis (2-hydroxypropyl)-ethylenediamine.

[0035] With regard to the metal anode 30, copper and tin were tested as metal anodes in the anode box, but both dissolved during electrolysis. Zinc was tested but polarized severely. A graphite electrode was also tested. The graphite decomposed, and the anode box became filled with graphite particles. Iridium oxide on titanium was tested, but there was significant deterioration of the coating during electrolysis.

[0036] The following Examples illustrate the present invention.

Example 1

[0037] The alkaline zinc-nickel bath was one gallon containing 10 g/liter of zinc, 1.5 g/liter of nickel, 20 g/liter of tetraethylenepentamine (TEPA) and 10g/liter of QUADROL. An anode box (disclosed in the Figure) having a NAFION 450 membrane on one side, containing 500 ml of a solution of 150g of sodium hydroxide was placed in the zinc-nickel bath. A metal anode was placed in the anode box. The metal anode was made of a coating of electroless nickel (containing 10% P) on steel. 5.0 Amperes of current were passed through the one-gallon cell for 6 hours. The plating bath was analyzed for cyanide, and no cyanide was detected. There was no erosion of the electroless coated steel anode in the anode box.

Comparative Example 2

[0038] In this comparative Example, the anode box was filled with a solution of 150g/liter of sodium hydroxide in water. The metal anode in the box was made of nickel metal. A one-gallon cell, similar to Example 1, was run at 5 amperes for 6 hours as before. The plating bath was analyzed for cyanide, and no cyanide was detected. The nickel anode had a thin conductive coating of nickel oxide/nickel hydroxide which did not interfere with the plating process.

[0039] There was no weight loss of nickel anode.

Example 3

[0040] The anode box of Example 1 was filled with a 20% solution of 50% liquid caustic. The metal anode was nickel electroplated from a Watts type plating solution, onto a steel base metal. The bath was run at 5 amperes

and 6.84 volts for 6 hours. The plating bath was analyzed for cyanide, and no cyanide was detected. There was no metal anode weight loss.

Example 4

[0041] A 1-gallon zinc-nickel plating bath, similar to the bath in Example 1, was electrolyzed for 100 ampere hours, using a box anode with a NAFION 450 ion exchange membrane covering one side of the box. The anode in the box was steel coated with electroless nickel with contained 8% P.

[0042] After 100 ampere hours, the bath was analyzed for cyanide and was found to contain no detectable cyanide. There was no metal anode weight loss.

Comparative Example 5

[0043] A 2-liter alkaline zinc-nickel plating bath containing 30g/liter of a polyethyleneimine (TEPA) was electrolyzed for 160 ampere hours with a nickel anode placed directly into the plating bath. The bath was found to contain 508 ppm of cyanide.

Example 6

[0044] The anode box of Example 1 was filled with a solution of 150g/liter of potassium hydroxide. The metal anode in the anolyte was a mild steel Q-panel. The bath, which was similar to the bath of Example 1, was electrolyzed at 5 amperes for 6 hours. There was a slight loss of weight from the steel anode. The electrolyte was analyzed for cyanide, and no cyanide was detected.

Comparative Example 7

[0045] The anode box of Example 1 is filled with a solution of 150g/liter of sodium hydroxide. The metal anode in the box is cobalt. The alkaline zinc-nickel bath contains 20 g/liter of poly (ethyleneimine) and is electrolyzed for 30 amp-hours.

Example 8

[0046] The metal anode in the anode box of Example 1 is steel coated with cobalt. The plating bath is similar to Example 1. The anolyte in the box is a 20% solution of 50% liquid caustic.

Comparative Example 9

[0047] The metal anode in the anode box in this comparative Example is a cobalt alloy anode. The anolyte is a 20% solution of 50% liquid caustic. The plating bath and apparatus are similar to Example 1.

Example 10

[0048] The metal anode in this Example is steel coated with a cobalt alloy coating from an electroless, cobalt-plating bath. The zinc-nickel plating bath and apparatus are similar to Example 1. The anode box contains a 15% solution of 50% liquid caustic. The alkaline zinc-nickel bath is electrolyzed for 6 hours at 5.0 amperes.

Example 11

[0049] In this Example, the metal anode in the anode box was stainless steel. The plating bath and apparatus were similar to Example 1. After 30-ampere hours, there was no detectable cyanide. There was no weight loss from the stainless steel anode.

[0050] By the present invention, an apparatus and process are provided by which zinc-nickel can be safely plated onto a substrate using an alkaline zinc-nickel electroplating bath containing polyamines, especially poly (alkyleneimines).

[0051] This is accomplished without anode erosion or generating cyanides in the electroplating bath.

[0052] It will be understood by those skilled in the art that a commercial apparatus and process will employ a zinc-nickel electroplating bath comprising additives in addition to a poly (alkyleneimine) such as other brighteners and sequestrants. In addition, a commercial bath typically can employ a 1000 gallon tank and the cathode workpiece positioned between arrays of compartmentalized anodes on opposite sides of the cathode along the sides of the tank.

[0053] From the above description of the invention, those skilled in the art will perceive improvements, changes and modifications. Such improvements, changes and modifications within the skill of the art are intended to be covered by the appended claims.

Claims

1. An apparatus for applying a zinc-nickel electroplate to a workpiece comprising: (a) a zinc-nickel electroplating bath comprising an amine additive and having a pH more than about 14; (b) a cathode workpiece in said bath; (c) an anode assembly in said bath comprising: (i) an enclosure defining an anolyte compartment, at least a portion of the enclosure being an ion exchange membrane; (ii) an anolyte in said compartment; and (iii) an insoluble metal anode immersed in said anolyte; wherein the anolyte is a sodium or potassium hydroxide solution comprising 50 to about 760 grams per liter sodium or potassium hydroxide and the anode is a mild steel, a steel alloy, or an iron chromium alloy.
2. The apparatus of claim 1 wherein said amine additive is a poly (alkyleneimine).

3. The apparatus of claim 2 wherein said zinc-nickel bath comprises poly (ethyleneimines).
4. The apparatus of claim 1 wherein said anode is stainless steel.
5. A process for applying a zinc-nickel electroplate to a workpiece comprising the steps of: (a) providing the apparatus of claim 1 ; and (b) applying a potential to the anode and cathode workpiece of said apparatus to cause a current flow from the anode to the cathode and plating of said workpiece.
6. A process for applying a zinc-nickel electroplate to a workpiece comprising the steps of: (a) providing a zinc-nickel electroplating bath comprising an amine additive and having a pH more than about 14; (b) positioning a cathode workpiece in said bath; (c) providing an anode assembly in said bath comprising: (i) an enclosure defining an anolyte compartment, at least a portion of said enclosure being an ion exchange membrane; (ii) an anolyte in said compartment; and (iii) an insoluble metal anode immersed in said anolyte, wherein the anolyte is a sodium or potassium hydroxide solution comprising 50 to about 760 grams per liter sodium or potassium hydroxide and the anode is a mild steel, a steel alloy, or an iron chromium alloy, (d) applying a potential to said anode and cathode to cause a current flow from the anode to the cathode through said ion exchange membrane.
7. The process of claim 6 wherein said amine additive is poly (alkyleneimine).
8. The process of claim 7 wherein said zinc-nickel bath comprises poly (ethyleneimine).
9. A process according to claim 6 wherein said anode is stainless steel.

Patentansprüche

1. Eine Vorrichtung zum Auftragen einer Zink-Nickel-Elektroplattierung auf ein Werkstück, die Folgendes aufweist:
 - (a) ein Zink-Nickel-Elektroplattierungsbad bzw. -Galvanisierbad, das einen Aminzusatz aufweist und einen pH-Wert von mehr als etwa 14 besitzt;
 - (b) ein Kathoden-Werkstück in dem Bad;
 - (c) eine Anodenanordnung in dem Bad, die Folgendes aufweist:
 - (I) eine Umschließung, die ein Anolytenteil definiert, wobei zumindest ein Teil der Um-

- schließung eine Ionenaustauschmembran ist;
 (II) ein Anolyt in dem Abteil;
 (III) eine Anode aus unlöslichem Metall, die in das Anolyt eingetaucht ist; 5
- wobei das Anolyt eine Natrium- oder Kaliumhydroxidlösung ist, die 50 bis etwa 760 Gramm pro Liter an Natrium- oder Kaliumhydroxid aufweist, und wobei die Anode ein kohlenstoffarmer Stahl bzw. Weichstahl, eine Stahllegierung oder eine Eisen-Chrom-Legierung ist. 10
2. Vorrichtung gemäß Anspruch 1, wobei der Aminzusatz ein Poly(alkylenimin) ist. 15
3. Vorrichtung gemäß Anspruch 2, wobei das Zink-Nickel-Bad Poly(ethylenimine) aufweist.
4. Vorrichtung gemäß Anspruch 1, wobei die Anode rostfreier Stahl ist. 20
5. Ein Verfahren zum Auftragen einer Zink-Nickel-Elektroplattierung auf ein Werkstück, wobei das Verfahren folgende Schritte aufweist: 25
- (a) Vorsehen der Vorrichtung gemäß Anspruch 1; und
 (b) Anlegen eines Potentials an die Anode und das Kathoden-Werkstück der Vorrichtung, um einen Stromfluss von der Anode zu der Kathode zu bewirken und das Werkstück zu plattieren bzw. galvanisieren. 30
6. Verfahren zum Auftragen einer Zink-Nickel-Elektroplattierung auf ein Werkstück, wobei das Verfahren folgende Schritte aufweist: 35
- (a) Vorsehen eines Zink-Nickel-Elektroplattierungsbad, das einen Aminzusatz aufweist und einen pH-Wert von mehr als etwa 14 besitzt;
 (b) Positionieren eines Kathoden-Werkstücks in dem Bad;
 (c) Vorsehen einer Anodenanordnung in dem Bad, die Folgendes umfasst: 45
- (I) eine Umschließung, die ein Anolytabteil definiert, wobei zumindest ein Teil der Umschließung eine Ionenaustauschmembran ist; 50
 (II) ein Anolyt in dem Abteil; und
 (III) eine Anode aus unlöslichem Metall, die in das Anolyt eingetaucht ist;
- wobei das Anolyt eine Natrium- oder Kaliumhydroxidlösung ist, die 50 bis etwa 760 Gramm pro Liter an Natrium- oder Kaliumhydroxid aufweist, und wobei die Anode ein kohlenstoffarmer Stahl bzw. Weichstahl, eine Stahllegierung oder eine Eisen-Chrom-Legierung ist; 55
- (d) Anlegen eines Potentials an die Anode und die Kathode, um einen Stromfluss durch die Ionenaustauschmembran von der Anode zur Kathode zu bewirken.
7. Verfahren gemäß Anspruch 6, wobei der Aminzusatz Poly(alkylenimin) ist.
8. Verfahren gemäß Anspruch 7, wobei das Zink-Nickel-Bad Poly(ethylenimin) aufweist.
9. Ein Verfahren gemäß Anspruch 6, wobei die Anode rostfreier Stahl ist.

Revendications

1. Appareil d'application d'un dépôt électrolytique de zinc-nickel sur une pièce comprenant : (a) un bain de dépôt électrolytique de zinc-nickel comprenant un additif amine et ayant un pH supérieur à environ 14 ; (b) une pièce de cathode dans le bain ; (c) un montage d'anode dans le bain comprenant :
 (i) une enceinte définissant un compartiment anolyte, au moins une partie de l'enceinte étant une membrane échangeuse d'ions ;
 (ii) un anolyte dans ledit compartiment ; et (iii) une anode métallique insoluble immergée dans l'anolyte ; dans lequel l'anolyte est une solution d'hydroxyde de sodium ou de potassium comprenant entre 50 et environ 760 g par litre d'hydroxyde de sodium ou de potassium et l'anode est en acier doux, en un alliage d'acier, ou en un alliage fer-chrome.
2. Appareil selon la revendication 1, dans lequel l'additif amine est une poly(alkylène-imine).
3. Appareil selon la revendication 2, dans lequel le bain de zinc-nickel comprend une poly(éthylène-imine).
4. Appareil selon la revendication 1, dans lequel l'anode est en acier inoxydable.
5. Procédé d'application d'un dépôt électrolytique sur une pièce comprenant les étapes suivantes : (a) prévoir l'appareil de la revendication 1 ; et (b) appliquer un potentiel à l'anode et à la pièce de cathode de l'appareil pour amener un courant à circuler de l'anode vers la cathode et à revêtir la pièce.
6. Procédé d'application d'un dépôt électrolytique de zinc-nickel sur une pièce comprenant les étapes suivantes : (a) prévoir un bain de dépôt électrolytique de zinc-nickel comprenant un additif amine ayant un

pH supérieur à environ 14 ; (b) disposer une pièce de cathode dans le bain ; (c) prévoir un montage d'anode dans le bain, comprenant : (i) une enceinte définissant un compartiment anolyte, au moins une partie de l'enceinte étant une membrane échangeuse d'ions ; (ii) un anolyte dans ledit compartiment ; et (iii) une anode métallique insoluble immergée dans l'anolyte, dans lequel l'anolyte est une solution d'hydroxyde de sodium ou de potassium comprenant entre 50 et environ 760 g par litre d'hydroxyde de sodium ou de potassium et l'anode est en acier doux, en un alliage d'acier, ou en un alliage fer-chrome, (d) appliquer un potentiel à l'anode et à la cathode pour amener un courant à circuler de l'anode vers la cathode à travers la membrane échangeuse d'ions.

7. Procédé selon la revendication 6, dans lequel l'additif amine est une poly(alkylène-imine).
8. Procédé selon la revendication 7, dans lequel le bain de zinc-nickel comprend une poly(éthylène-imine).
9. Procédé selon la revendication 6, dans lequel l'anode est en acier inoxydable.

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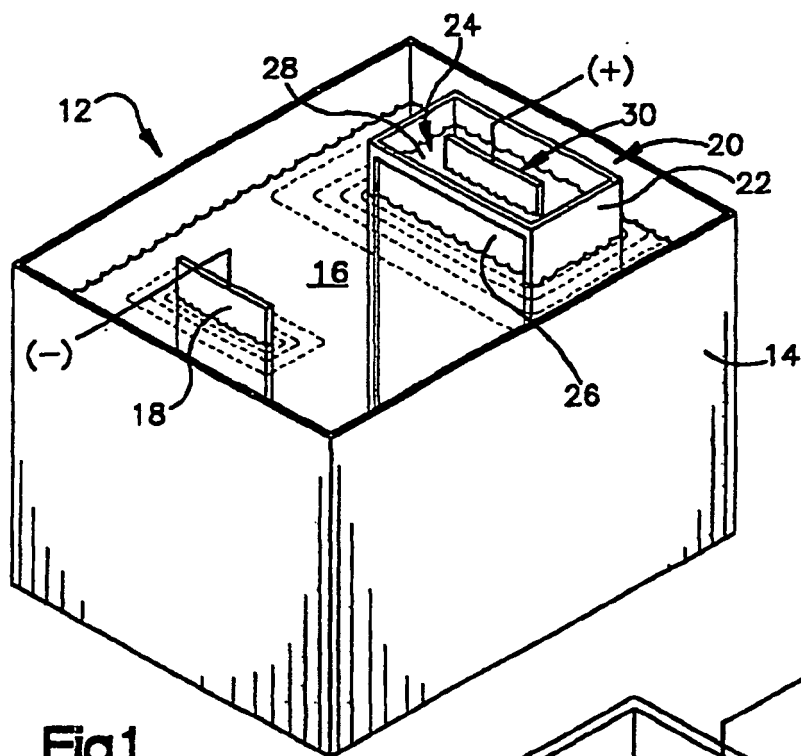


Fig.1

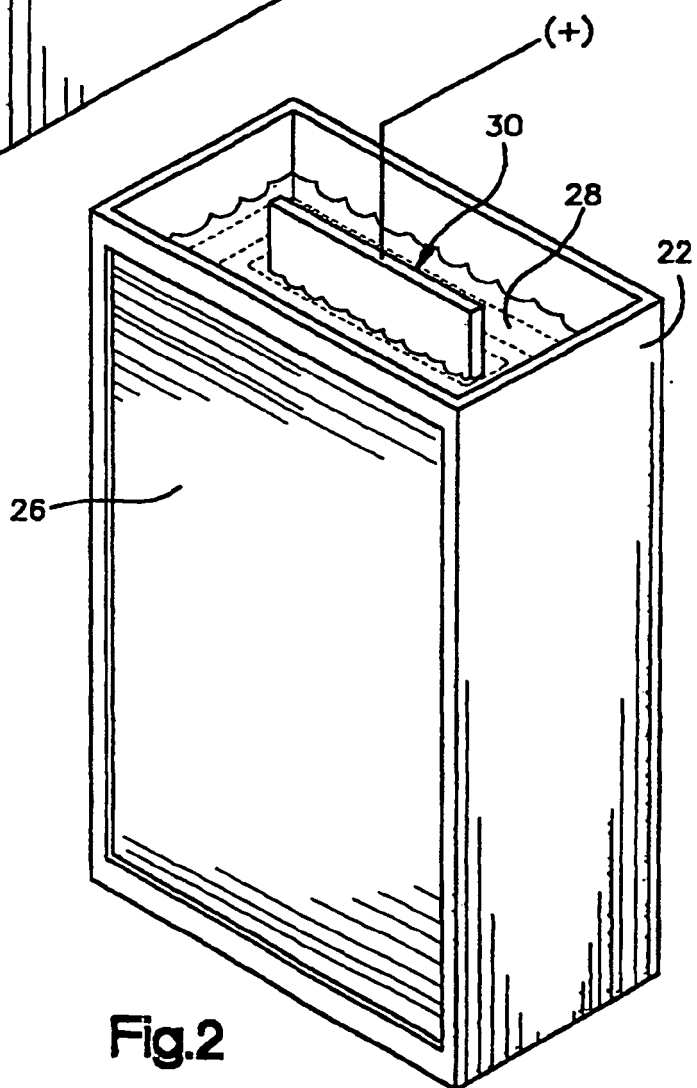


Fig.2

REFERENCES CITED IN THE DESCRIPTION

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