

METHOD OF PLATING ALUMINIUM

This invention relates to the metal plating of zincated aluminium and, more particularly, to providing an enhanced adhesive and smooth plating by employing an improved double zincating process and, preferably, in combination with a unique electroless metal plating procedure, utilizing a specially formulated electroless metal plating bath.

Metal plating of aluminium is of considerable commercial interest and one application is the preparation of memory disks which are used in a variety of electronic applications such as computer and data processing systems. Aluminium is the preferred substrate for the disk although other suitable metals may be employed. In general, a relatively thin layer of nonmagnetic electroless nickel is applied on the aluminium followed by a thin layer of a magnetic material such as cobalt. A signal is stored on the disk by magnetizing the cobalt layer to represent the signal at a selected moment in time.

Typical alloys used for memory disks are Aluminium Associated Numbers 5086 and 5586. These disks contain magnesium in an amount of about 4% by weight. Generally, the aluminium disks are about 1.25 to 5 mm. thick and contain, by weight, about 4% to 4.90% magnesium, 0.01% to 0.40% copper, 0.01% to 0.40% zinc, chromium, nickel, iron, silicon and the balance aluminium and inevitable impurities.

1 The completed metal plated disk must be extremely
2 smooth and uniform so as to prevent "crashing" against
3 magnetizing head of the device which flies extremely
4 close (generally 5-8 microinches) to the disk surface.
5 While the starting aluminium substrate must itself be
6 extremely smooth and flat as described in U.S. Patent
7 No. 4,825,680, the metal plating of the disk must
8 likewise be smooth and uniform so that the final disk
9 product meets the exacting specifications required of
10 these type products.

11

12 Unfortunately, however, metal plating of a substrate,
13 and even electroless metal plating, does not
14 necessarily produce a smooth coating. Plating voids,
15 inclusions, bridging and the like are only some of the
16 plating problems which can cause a rough disk surface
17 which is unacceptable.

18

19 Aluminium and its alloys also present additional
20 plating problems because of the rapidity with which
21 they form an oxide coating when exposed to air. As a
22 result, special treatments must be employed when
23 plating on aluminium. These treatments include
24 mechanical treatments; chemical etches, especially acid
25 etches containing iron, nickel, and manganese salts;
26 alkaline displacement solutions, especially those
27 depositing zinc, brass, and copper; anodizing,
28 especially in phosphoric, sulphuric or chromic acids;
29 and electroplating with zinc at low current densities
30 for a few seconds. Of these treatments, the alkaline
31 displacement solutions are generally the most
32 successful commercially.

33

1 While many metals can be deposited on aluminium by
2 displacement, zinc is the most common. In this case,
3 the process is known as the zincate process.

4
5 Over the years a number of improvements have been made
6 in the conventional zincate formulation and zincating
7 process, with most of them aimed at accelerating the
8 rate of film formation, and the degree of adhesion and
9 uniformity of the zinc coating produced. A detailed
10 summary of the zincating process may be found in Loch,
11 U.S. Patent No. 4,346,128, and Saubestre, U.S. Patent
12 No. 3,216,835.

13
14 In Loch, U.S. Patent No. 4,346,128, the process
15 involves soaking the zincated work piece in nitric acid
16 for from one to three minutes (instead of the usual
17 20-30 seconds) used to strip the zincate coating. This
18 procedure purportedly produces a thin uniform oxide
19 coating on the substrate that serves to further reduce
20 zinc deposition rates and to thereby provide better
21 zincate adhesion for the final (second) zincate
22 coating.

23
24 In the conventional zincating process, the aluminium is
25 prepared by alkaline cleaning to remove organic and
26 inorganic surface contaminations such as oil and
27 grease, followed by a cold water rinse. The cleaned
28 aluminium is then sufficiently etched to eliminate
29 solid impurities and alloying constituents which might
30 create voids resulting in bridging of subsequent
31 deposits. After a water rinse, the aluminium is
32 de-smutted to remove metallic residues and aluminium
33 oxides remaining on the surface. Thorough rinsing is

1 required and then the zincate coating is applied using
2 an immersion zinc bath to prevent re-oxidation of the
3 cleaned surface.

4
5 The zinc coating is obtained by immersion of the
6 aluminium part in an alkaline solution containing zinc
7 ions. The amount of zinc depends on the time and type
8 of immersion bath used, the aluminium alloy,
9 temperature of the solution and pretreatment process.
10 The zinc coating bath also functions as an etching
11 solution and any oxides reformed during the
12 transferring operations are dissolved by the alkaline
13 zincate while depositing zinc onto the aluminium.

14
15 The general procedure now followed by industry is to
16 double zincate whereby the first zinc film is removed
17 using nitric acid followed by application of a second
18 immersion zinc deposit. Double zincating is a
19 preferred method for plating aluminium and is
20 especially useful on certain difficult-to-plate
21 aluminium alloys to ensure better adhesion of the final
22 metal layer deposit.

23
24 Double zincate methods for preparing aluminium for
25 metal plating are well-known in the art as discussed.
26 In general, any aluminium alloy may be treated using
27 the present invention and exemplary alloys are 5086,
28 5586 and CZ-46. The aluminium may be wrought or cast.

29
30 While the specific double-zincate method employed may
31 vary according to the alloys treated and the claimed
32 results, all the methods use a HNO_3 acid dip to remove
33 the first zincate film and this is the step that the
34 present invention is concerned with.

1 The use of cadmium in electroless nickel plating baths
2 is described in U.S. Patent No. 2,929,742. Cadmium is
3 disclosed as affecting the hydrogen overvoltage and is
4 considered beneficial to improving the brightness of
5 the deposit. Amounts of up to 100 mg/l cadmium
6 chloride are shown.

7
8 Despite the acceptance and effectiveness of the double
9 zincating process, the need still exists for an
10 improved process providing both enhanced adhesion and
11 smoothness of the metal plating on the zincated
12 aluminium substrate. Without being limited to theory,
13 it is believed that the properties of the metal plate
14 are directly related to the thickness, uniformity and
15 continuity of the zincate coating with thinner coatings
16 generally providing a smoother and more adhesive metal
17 plating.

18
19 The present invention seeks to provide a method for
20 preparing aluminium substrate articles that may have
21 extremely smooth metal plated coatings.

22
23 The present invention also seeks to provide an improved
24 double zincating process for the metal plating of
25 aluminium, which improved process provides a thinner,
26 more uniform, and continuous zincate coating and
27 produces enhanced adhesive metal plating deposits and
28 metal plating smoothness.

29
30 The invention additionally seeks to provide an improved
31 electroless metal plating composition and plating
32 method for coating zincated aluminium substrates with
33 extremely smooth coatings.

1 Other objects and advantages may become apparent from
2 the following description.

3

4 Thus according to a first aspect of the present
5 invention there is provided a method of forming a metal
6 coating on an aluminium substrate, the method
7 comprising:

8 (a) forming a zinc or zinc alloy deposit on the
9 substrate;

10 (b) contacting the substrate with a zinc removing
11 composition containing a source of Group VIII (in this
12 specification of the Mendeleef Periodic Table) metal
13 ions; and

14 (c) optionally repeating (a).

15

16 It is preferred that (c) is not optional; that is to
17 say, the zincating stages (a) and (c) are both
18 included: this is known as a "double zincating"
19 process.

20

21 In one, or both, of the zincating stages (a) and/or (c)
22 the zinc or zinc alloy is preferably formed by
23 contacting the substrate with a zinc or zinc alloy
24 plating composition. Such a composition suitably
25 comprises a source of zinc ions, an alkali and
26 optionally a source of metal alloy ions.

27

28 Here the term "aluminium", in relation to a substrate,
29 encompasses substrates made only of aluminium, mostly
30 aluminium (Al is the major component) and aluminium
31 alloys (e.g. with any combination of Mg, Cu, Zn, Cr, Ni
32 and/or Fe). Other elements may be present in the
33 substrate e.g. silicon. Preferred substrate are
34 aluminium disks (e.g. memory disks).

1 A preferred process according to the present invention
2 comprises:

- 3
- 4 (a) optionally cleaning an aluminium substrate, such
5 as by contacting the aluminium substrate with an
6 alkaline (and suitably non-etch) cleaner, for example a
7 non-silicated alkaline cleaner;
- 8 (b) optionally etching the aluminium substrate, such
9 as by contacting the aluminium substrate with a
10 (preferably acidic) etchant;
- 11 (c) optionally de-smutting the aluminium substrate
12 such as by contacting the aluminium substrate with a
13 (preferably acidic) de-smutting agent, for example one
14 that contains nitric acid and/or sulphuric acid and
15 optionally a fluoride salt;
- 16 (d) forming a zinc or zinc alloy deposit on the
17 aluminium substrate (such as by forming a zincate
18 coating) such as by using a zinc or zinc alloy plating
19 composition comprising a source of zinc ions, an alkali
20 (preferably a hydroxide) and optionally a chelating
21 agent, a wetting agent (e.g. anionic) and/or a metallic
22 additive (such as a source of metal ions other than
23 zinc, such as iron (e.g. Fe^{3+}));
- 24 (e) contacting the aluminium substrate with a (zinc
25 removing) composition comprising nitric acid and a
26 source of Group VIII ions (such as ferric ions);
- 27 (f) repeating stage (d), to apply a zincate coating on
28 the aluminium substrate;
- 29 (g) forming a metal coating, preferably other than
30 zinc, (such as a nickel or nickel alloy deposit) on the
31 aluminium substrate, preferably by electroless plating,
32 such as for example using a metal (e.g. nickel or
33 nickel alloy) electroless plating composition

1 comprising a source of metal (e.g. nickel) ions, a
2 source of cadmium ions, a reducing agent and preferably
3 a complexing or chelating agent; and

4 (h) optionally repeating (g) to provide an additional
5 metal coating, which is preferably thicker than the
6 coating formed in (g).

7

8 In preferred methods (a), (b), (c) and (h) are not
9 optional.

10

11 It has been found that extremely smooth metal plated
12 aluminium substrates, e.g., memory disks, can be made
13 by preferably employing a special double zincating
14 process in conjunction with an electroless metal
15 plating bath containing an effective amount of cadmium.
16 The double zincating process for preparing aluminium
17 and aluminium alloys for metal plating can be improved
18 by utilizing a specially formulated HNO_3 bath to strip
19 the first zincate film from the aluminium. The
20 stripped aluminium may then be water rinsed and coated
21 with a second zincate film. Broadly stated, the HNO_3
22 bath used to strip the zincate coating preferably
23 comprises a source of at least one Group VIII ion,
24 preferably a source of ferric ions (in an effective
25 amount) for example, present at from 0.1 g/l to 2 g/l
26 and HNO_3 in an amount of from 250 or 350 to 600 g/l or
27 higher.

28

29 Following the zincate procedure, an electroless metal,
30 e.g., nickel, plating of the aluminium can be improved
31 by employing an electroless metal plating bath
32 containing an effective amount of a source of cadmium
33 (ions) to provide an extremely smooth metal coating.
34 Broadly stated, the electroless metal bath preferably
35 comprises:

- 1 (1) a source of metal (eg nickel) ions;
- 2 (2) a reducing agent such as a hypophosphite and/or an
- 3 amine borane;
- 4 (3) an acid or alkali (eg hydroxide) pH adjuster to
- 5 provide the required pH;
- 6 (4) a complexing agent for the metal ions sufficient
- 7 to prevent their precipitation in solution; and
- 8 (5) an effective amount of cadmium ions (to provide
- 9 the extremely smooth coating of the invention).

10

11 Suitably the cadmium level is from 0.1 to 1 mg/l, with
12 a preferred level being from 0.4 to 0.7 mg/l.

13

14 The invention may thus use a cadmium containing
15 electroless plating bath as hereinbefore described to
16 provide an enhanced smooth coating on a zincated
17 aluminium substrate.

18

19 It has been found that the consumption of the cadmium
20 can occur rapidly in the first stages of plating, but
21 at about 10 minutes and thereafter the consumption can
22 be very slow and the presence of the cadmium may not be
23 important during further plating. Thus a preferred
24 mode of operation is to start the plating of the
25 zincated aluminium substrate in an electroless bath
26 containing an effective amount of cadmium, for example
27 from 0.1 to 1 mg/l, and not to replenish the cadmium
28 until a new zincated substrate is to be plated in the
29 bath.

30

31 The electroless metal plating bath suitably also
32 contains a source of metal ions; a reducing agent; a
33 chelator, and/or a pH adjuster. These components are

1 conventionally replenished by measuring the
2 concentration of the component and adding more of the
3 component, as needed, to maintain the level between
4 desired operating limits. Present plating methods that
5 use automatic controllers which continually measure and
6 replenish the bath components are suitable (a
7 continuous dynamic replenishment process). Other
8 methods, such as manual measuring and replenishment at
9 certain intervals, e.g., hourly, etc., may also be
10 employed.

11

12 The invention encompasses a double zincating process
13 for preparing aluminium and aluminium alloys for metal
14 plating wherein the aluminium after pretreatment is
15 zincated by immersion in a zincating bath, the zincated
16 aluminium is then dipped in a nitric bath to remove the
17 zincate coating, followed by immersion in a zincating
18 bath to coat the aluminium and metal plating of the
19 zincated aluminium. One employs in the nitric acid
20 bath, an effective amount of a Group VIII ion.

21

22 The invention method can involve depositing a smooth
23 electroless metal coating on a zincated aluminium
24 substrate comprising coating a thin first layer of the
25 metal on the substrate using an electroless metal
26 plating bath containing cadmium, followed by the use of
27 a different electroless metal plating bath to plate the
28 substrate with a second metal coating to the desired
29 thickness, with the thickness of the second metal
30 coating being thicker than the first metal coating.

31 The invention additionally contemplates a method for
32 depositing a smooth electroless metal coating on a
33 zincated aluminium substrate wherein the zincated

1 substrate is immersed in an electroless metal plating
2 bath to plate a coating of a desired thickness and the
3 bath contains metal ions and a reducing agent which
4 components are controlled within desired operating
5 limits by periodic replenishment the improvement
6 comprising utilizing an effective amount of cadmium in
7 the bath at the start of the plating operation and not
8 replenishing the cadmium to the desired operating level
9 until the plating operation is finished and/or new,
10 unplated zincated aluminium substrates are immersed in
11 the bath for plating.

12

13 In a highly preferred embodiment, multiple plating
14 baths can be employed whereby a thin coating of nickel
15 is provided on the zincated surface from an electroless
16 bath containing a source of cadmium ions followed by
17 plating a thicker, final coating (such as also of
18 nickel) from a second (e.g. conventional) electroless
19 plating bath. This preferred process is similar to the
20 process described in U.S. Patent No. 4,567,066 granted
21 to P.B. Schultz and E.F. Yarkosky.

22

23 A preferred process of the present invention is
24 described as follows. It should be understood that
25 water rinses are preferably employed after each stage.

26

27 A first stage in the process is usually to clean the
28 aluminium substrate surface, of grease and oil with an
29 alkaline (non-etch) cleaner, such as ENBOND (Registered
30 Trade Mark) NS-35 sold by Enthone, Incorporated, West
31 Haven, Connecticut. ENBOND NS-35 is a nonsilicated
32 mildly alkaline cleaner. This is suitable for use
33 (i.e. contact with the aluminium substrate) over a

1 temperature range of from 49°C to 66°C, e.g. 60-63°C
2 preferably for 1 to 5 or 6 minutes.

3
4 Etching of the cleaned aluminium substrate may then be
5 performed using etchants such as ACTANE (Registered
6 Trade Mark) E-10, ENBOND E-14 or ENBOND E-24, all of
7 which are sold by Enthone. These materials are either
8 acidic or alkaline. However, an acid etchant is
9 generally preferred, particularly when surface
10 dimensions, tolerances and integrity are important.
11 The etchants are preferably used (i.e. contacted with
12 the aluminium substrate) at elevated temperatures, such
13 as from 49°C to 66°C, e.g. 60-63°C, preferably for from
14 1 to 3 minutes.

15
16 De-smutting of the aluminium substrate may be performed
17 using a HNO_3 solution (for example 50% by volume) or
18 mixtures of HNO_3 and H_2SO_4 alone (e.g. a 50/50
19 solution) or in combination with ACTANE 70 sold by
20 Enthone. ACTANE 70 is an acidic, fluoride salt product
21 containing ammonium bifluoride. A preferred
22 de-smutting solution contains 25% by volume H_2SO_4 , 50%
23 by volume HNO_3 and 1 lb/gallon ACTANE 70 in water.
24 This may be performed at about room temperature for
25 from 30-90 seconds, e.g. about 1 minute.

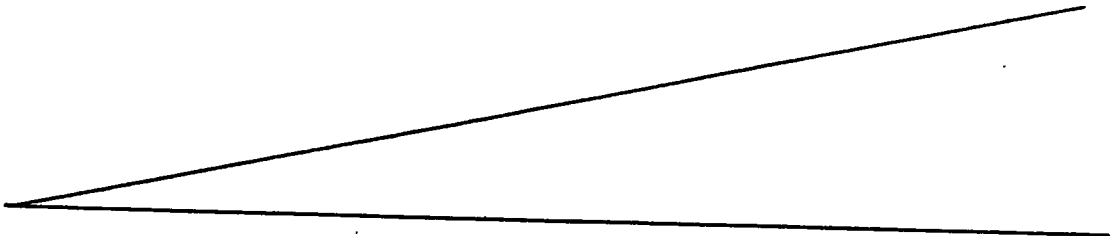
26
27 It is at this point that a zincate coating can be
28 applied to the aluminium by immersion in a zincate bath
29 as described in Saubestre, U.S. Patent No. 3,216,835,
30 supra. A preferred bath, due to its demonstrated
31 effectiveness, is ALUMON (Registered Trade Mark) EN
32 sold by Enthone. ALUMON EN contains an alkali metal
33 hydroxide, a zinc compound or salt (such as zinc oxide
34 and/or zinc sulphate), a chelating agent and optionally
35 an anionic wetting agent _____

1 and/or a metallic additive (e.g. Fe^{3+} ions). The
2 composition is preferably at about room temperature
3 when contacted with the aluminium substrate.
4

5 An article by D.S. Lashmore entitled "Immersion
6 Coatings on Aluminium", Plating and Surface Finishing,
7 67, pages 36-42 (1980) shows the use of iron (e.g.,
8 ferric chloride) in the zincate solution to deposit
9 iron along with the zinc and produce a more adhesive
10 zincate coating which can be very resistant and
11 comparatively insoluble in HNO_3 . ALUMON EN and other
12 commercial zincate solutions contain iron.
13

14 Generally, a double zincate process involves immersion
15 of the aluminium substrate in a (dilute) zincate
16 plating composition or bath (such as an ALUMON EN) for
17 a period of from 20-50 seconds, suitably followed by a
18 thorough cold water rinse, a zinc removing operation
19 with nitric acid, preferably a further cold water
20 rinse, and a second zincate immersion and
21 advantageously a subsequent rinse.
22

23 In contrast to the Loch procedure, the present
24 invention involves the use of a source of Group VIII
25 ions, e.g., ferric ions, in the nitric acid bath. This
26 accomplishes a similar result of reducing zinc
27 deposition rates while providing a zincate coating
28 which may be very adhesive, uniform and continuous and
29
30
31
32
33



1 on which an extremely smooth metal plating may be
2 coated.

3
4 The nitric acid composition used to strip the (e.g.
5 first) zincate coating is preferably a 50% by volume
6 solution. This may have a concentration range of from
7 350 to 600 g/l, and preferably from 450 to 550 g/l.
8 The composition also contains a source of Group VIII
9 ions, preferably a source of ferric ions. This is
10 suitably provided in an amount of from 0.1 g/l to 1 or
11 2 g/l, preferably 0.3 g/l to 0.8 g/l and most
12 preferably 0.4 g/l to 0.6 g/l. At levels below about
13 0.1 g/l, minimal effects may be obtained while at
14 levels below about 0.1 g/l, minimal effects may be
15 obtained while at levels above about 2 g/l, the surface
16 topography may be severely affected.

17
18 The nitric acid zinc removing composition may be
19 employed (that is to say contacted with the aluminium
20 substrate) at any suitable temperature, although it is
21 preferred that this is from 20°C to 25°C or higher but
22 preferably 21°C to 23°C. Contact (suitably immersion)
23 times suitably range from 30 to 90 seconds, preferably
24 from 40 to 60 seconds.

25
26 Exemplary Group VIII ions which may be employed include
27 iron, nickel and cobalt. Ferric ions are particularly
28 preferred.

29
30 It will be understood by those skilled in the art that
31 the concentration, composition temperature and contact
32 (immersion) time are interrelated and that, in general,
33 the higher the temperature and concentration, the

1 shorter the contact (immersion) time necessary to
2 achieve the desired surface effect, and the use of
3 Group VIII ions in the bath may provide enhanced
4 adhesion and smoothness of the metal plating.

5
6 While other metals may now be plated on the specially
7 prepared zinc coated aluminium substrate, the following
8 description, although applicable to any suitable metal,
9 may specifically reference nickel, as illustrative
10 because of its commercial importance.

11
12 Electroless nickel plating compositions for applying
13 nickel coatings (that is to say, nickel and nickel
14 alloy deposits) are well known in the art and plating
15 processes and compositions are described in numerous
16 publications. For example, compositions for depositing
17 electroless nickel are described in U.S. Patent Nos.
18 2,690,401; 2,690,402; 2,762,723; 2,935,425; 2,929,742;
19 and 3,338,726. Other useful compositions for
20 depositing nickel and nickel alloys are disclosed in
21 the 35th Annual Edition of the Metal Finish Guidebook
22 for 1967, Metal and plastics publications Inc.,
23 Westwood, N.J., pages 483-486.

24
25 Preferred electroless metal, e.g. nickel, electroless
26 plating compositions are aqueous and suitably comprise
27 at least four ingredients dissolved in a solvent,
28 typically water. They are:

- 29 (1) a source of metal, e.g. nickel, ions;
30 (2) a reducing agent such as a hypophosphite,
31 borohydride, hydrazine or an amine borane;
32 (3) an acid or hydroxide pH adjuster to provide the
33 required pH;

1 (4) preferably a complexing or chelating agent for the
2 metal ions, suitably in a sufficient amount to prevent
3 metal ion precipitation in solution; and

4 (5) a source of cadmium ions.

5 A large number of suitable complexing agents for
6 electroless nickel solutions are described in the above
7 noted publications. It will be appreciated by those
8 skilled in the art that the nickel, or other metal
9 being applied, will usually be in the form of an alloy
10 with other materials present in the bath. Thus, if
11 hypophosphite is used as the reducing agent, the
12 deposit will usually contain nickel and phosphorous.
13 Similarly, if an amine borane is employed, the deposit
14 will usually contain nickel and boron. Thus, use of
15 the term "nickel" includes the other elements, such as
16 S and P, normally deposited therewith.

17

18 The source of metal, e.g. nickel, ions may be provided
19 by any suitable soluble salt such as a sulphate,
20 chloride, acetate and mixtures thereof. The
21 concentration of the metal, such as nickel, in solution
22 may vary widely and is preferably from 0.1 to 100 g/l,
23 such as from 2 to 50 g/l, e.g. 2 to 10 or 30 g/l.

24

25 The reducing agent, especially when the aluminium
26 substrate is a memory disk, is usually the
27 hypophosphite ion. This may be supplied to the bath by
28 any suitable source such as an alkali metal (e.g.
29 sodium or potassium) ammonium, and/or metal, e.g.,
30 nickel, hypophosphite. Other reducing agents such as
31 amine boranes, borohydrides and hydrazine may also
32 suitably be employed. The concentration of the
33 reducing agent is preferably in excess of the amount

1 sufficient to reduce the amount of metal ions, e.g.
2 nickel present in the bath.

3
4 The metal plating composition can be acid, neutral or
5 alkaline. An acid or alkaline pH adjuster may be
6 selected from a wide range of materials such as
7 hydroxides (e.g. ammonium hydroxide or alkali metal,
8 e.g. sodium, hydroxide) and mineral acids, e.g.
9 hydrochloric acid, and the like. The pH of the bath
10 may range from 2 to 12; acids baths are preferred. A
11 pH range of 4 to 5, e.g., 4.3 to 4.6, is preferred,
12 both for the cadmium contained in the bath when
13 depositing the metal coating on the zincate layer, such
14 as depositing a final layer of nickel when the cadmium
15 containing bath is used to provide only a thin, strike
16 coating.

17
18 The complexing (or chelating) agent may be selected
19 from a wide variety of materials such as carboxylic
20 acids, lactic acid, malic acid and those containing
21 anions such as acetate, citrate, glycollate,
22 pyrophosphate and the like, with mixtures thereof also
23 being suitable. Ranges for the complexing agent, based
24 on the anion, may vary widely, for example, from 1 to
25 300 g/l, preferably from 5 to 50 g/l.

26
27 The electroless metal plating compositions may also
28 contain other ingredients known in the art such as
29 buffering agents, bath stabilizers, rate promoters,
30 brighteners, etc. Stabilizers such as lead, antimony,
31 mercury, tin and oxy compounds such as iodate may also
32 be employed.

33

1 A suitable plating composition may be formed by
2 dissolving the ingredients in water and adjusting the
3 pH to the desired range.

4
5 The zinc coated aluminium substrate may be plated with
6 the electroless metal, e.g. nickel-cadmium, to the
7 desired final thickness. Preferably, the substrate is
8 contacted with the plating composition by immersion in
9 the composition. One may then plate a thin metal, e.g.
10 nickel, coating adequate to provide a suitable base for
11 the extremely smooth thick deposits of a final metal,
12 e.g. nickel, plate, for example using a different
13 electroless metal, e.g. nickel, plating composition.

14
15 The metal deposited using the metal plating composition
16 (or first metal coating if there are two) preferably
17 has a thickness range up to about 0.1 mil, or higher,
18 with from 0.005 to 0.08 mils, e.g. from 0.01 to 0.05,
19 being preferred. An immersion time of 15 seconds to 15
20 minutes will usually provide the desired coating,
21 depending on composition parameters. A temperature
22 range of from 25°C to boiling, e.g., 100°C, may be
23 employed, with a range of from 30°C to 95°C being
24 preferred.

25
26 A next stage in the preferred procedure is to complete
27 the metal plating to the desired thickness and physical
28 characteristics by immersing the metal, e.g. nickel
29 coated substrate in another electroless nickel plating
30 bath, (which may be the same or different, from that
31 used to form the first metal coating) which is
32 preferably maintained at a temperature ranging from
33 30°C to 100°C, e.g. boiling, preferably from 80°C to

1 95°C. A thickness up to 5 mils, or higher may be
2 achieved, with a range of from 0.1 to 2 mils being
3 preferable for most applications. When this "strike
4 bath" process is used, it is preferred not to rinse the
5 strike coated aluminium substrate before immersion of
6 the substrate in the next, i.e. second and usually
7 final plating composition.

8
9 The cadmium ions may be provided by the use of any
10 soluble cadmium source such as a cadmium salt, e.g.
11 cadmium sulphate. It is important to control the
12 cadmium concentration to obtain the extremely smooth
13 coatings of the invention and a suitable effective
14 level is from 0.1 to 1 mg/l, preferably 0.3 to 0.8 mg/l
15 and most preferably 0.5 to 0.7 mg/l. Amounts as high
16 as 2 or 3 mg/l or higher may be used for certain
17 applications not requiring as smooth a surface as for
18 memory disks.

19
20 It will be appreciated by those skilled in the art that
21 the rate of plating may be influenced by many factors
22 including:

- 23 (1) pH of the plating solution;
- 24 (2) concentration of reductant;
- 25 (3) the temperature of the plating composition;
- 26 (4) concentration of soluble metal, e.g. nickel;
- 27 (5) ratio of the volume of composition to the area
28 plated;
- 29 (6) presence of soluble fluoride salts (rate
30 promoters); and
- 31 (7) presence of wetting agent and/or agitation,
- 32 and that the above parameters are only provided to give
33 general guidance for practising the invention.

1 The stage (g) of forming the metal coating may be
2 repeated more than once, for example, twice. In this
3 latter case it is preferred that the second metal
4 coating is thicker than the first.

5
6 Although the cadmium may be replenished periodically,
7 it is not replenished (such as to a desired operating
8 level) until the plating (operation) is completed
9 and/or new aluminium substrates (zincated ones) are
10 contacted with the composition (such as by immersion)
11 for electroless plating.

12

13 A second aspect of the present invention relates to an
14 aluminium substrate having a metal coating formed
15 according to a method of the first aspect. Preferred
16 features and characteristics for the third aspect are
17 as for the first aspect mutatis mutandis.

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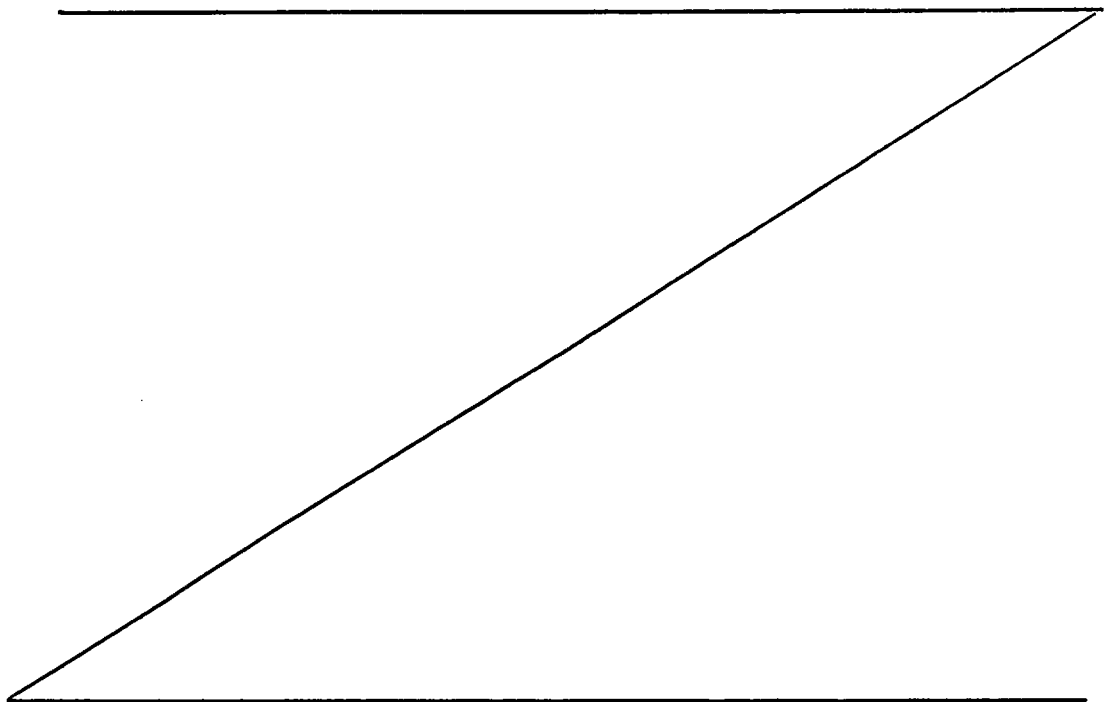
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1 The invention may be illustrated by way of example with
2 reference to the accompanying drawings, in which:

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4 FIGURES 1A and 2A (PRIOR ART) are photomicrographs at
5 magnification 500X of electrolessly nickel plated
6 aluminium substrates which were prepared for plating
7 using a conventional, prior art double zincate process;

8
9 FIGURES 1B and 2B are photomicrographs at
10 magnification 500X of electrolessly nickel plated
11 aluminium substrates which were prepared for plating
12 using a double zincate process according to the present
13 invention;

14
15 FIGURE 3 is a graph showing that a nitric acid
16 stripping solution according to the present invention
17 (containing Fe^{+++} ions) removes more zinc from a
18 zincated aluminium substrate than a conventional, prior
19 art zincate nitric acid solution;

20
21 FIGURE 4 is a graph showing that aluminium substrates
22 prepared according to the present invention have less
23 zinc on the surface to be metal plated (a thinner
24 coating) than substrates prepared using a conventional,
25 prior art, double zincate process;

26
27 FIGURE 5A is a photomicrograph at magnification 500X
28 of an electrolessly nickel plated aluminium substrate
29 using a conventional, prior art, zincating and plating
30 procedure; and

31
32 FIGURES 5B, 5C and 5D are photomicrographs at
33 magnification 500X of an electrolessly nickel plated

1 aluminium substrate using a zincating and/or plating
2 process according to the present invention.

3
4 The invention will now be described by way of example,
5 with reference to the following Examples, which are
6 provided for the purposes of illustration and are not
7 intended to be construed as being limiting on the
8 present invention. In the following specific examples
9 (which are illustrative and in no way limitative) all
10 parts and percentages are by weight and temperatures in
11 degrees centigrade unless otherwise specified.

12

13 COMPARATIVE EXAMPLE IA AND EXAMPLE IB

14

15 IA. CZ-46 aluminium alloy disks were double zincated
16 and plated with electroless nickel using the following
17 procedure (a cold water rinse followed each of the
18 steps):

19

- 20 (1) Immerse in ENBOND NS-35 (alkaline cleaner) for 3
21 minutes at 60°C;
22 (2) Immerse in ACTANE E-10 (etchant) for 1 minute at
23 60°C;
24 (3) Immerse in 50% by volume HNO₃ for 1 minute at room
25 temperature (to de-smut);
26 (4) Immerse in ALUMON (Registered Trade Mark) EN
27 (first zincate) for 35 seconds at room temperature;
28 (5) Immerse in 50% by volume HNO₃ (zinc remover) for 1
29 minute at room temperature;
30 (6) Immerse in ALUMON EN (second zincate for 16
31 seconds at room temperature;
32 (7) Immerse in ENPLATE (Registered Trade Mark) ADP-300
33 (nickel plating composition) for 1 hour at 84-87°C (pH
34 4.5 ± 0.1).

1 ENPLATE ADP-300 is an acidic based (pH4.6) electroless
2 nickel plating bath containing, in g/l, nickel sulphate
3 hexahydrate (26), sodium hypophosphite (20), sodium
4 lactate (60%) (71), malic acid (11.8), sodium hydroxide
5 (4.6), potassium iodate (0.015), lead nitrate (0.0003)
6 and an anionic surfactant (0.02).

7
8 FIGURE 1A shows the nickel surface resulting from
9 using the above conventional, prior art, double
10 zincating procedure.

11
12 IB. When the same procedure was used except that
13 ferric ions (as ferric chloride) were added to the HNO_3
14 in step (5) at a level of 0.5 g/l Fe^{+++} , a markedly
15 smoother nickel surface was obtained as shown in FIGURE
16 1B.

17
18 COMPARATIVE EXAMPLE IIA AND EXAMPLE IIB

19
20 IIA. A procedure similar to COMPARATIVE EXAMPLE I was
21 conducted on 5586 aluminium alloy disks as follows:

- 22
23 (1) Immerse in ENBOND NS-35 (alkali cleaner) for 5
24 minutes at 63°C;
25 (2) Immerse in ACTANE E-10 (etchant) for 2 minutes at
26 63°C;
27 (3) Immerse in 50% by volume HNO_3 for 1 minute at room
28 temperature (to de-smut);
29 (4) Immerse in ALUMON EN (first zincate) for 45
30 seconds at room temperature;
31 (5) Immerse in 50% by volume HNO_3 (zinc remover) for
32 30 seconds at room temperature;
33 (6) Immerse in ALUMON EN (second zincate) for 15
34 seconds at room temperature;

1 (7) Immerse in ENPLATE ADP-300 (nickel plating
2 composition) for 2 hours at 84-87°C (pH 4.5 ± 0.1).
3

4 FIGURE 2A shows the nickel surface resulting from
5 using the above conventional, prior art, double
6 zincating procedure.
7

8 IIB. When the same procedure was used except that
9 ferric ions were added to the HNO₃ in step (5) at a
10 level of 0.5 g/l, a markedly smoother nickel surface
11 was obtained as shown by FIGURE 2B.
12

13 COMPARATIVE EXAMPLE IIIA AND EXAMPLE IIIB
14

15 IIIA. The procedure of COMPARATIVE EXAMPLE I (steps
16 (1) - (4) was followed to prepare a number of zincated
17 CZ-46 aluminium alloy disks.
18

19 The disks were chosen at random and a total of 40 ft²
20 was stripped at room temperature for each HNO₃ bath
21 tested. The control HNO₃ was 50% by volume.
22

23 IIIB. Here an HNO₃ composition of the present
24 invention was used which was 50% by volume and
25 contained 0.50 g/l ferric ions (supplied as ferric
26 chloride).
27

28 FIGURE 3 shows the amount of zinc coating removed per
29 square feet of disk stripped and the results clearly
30 show that the HNO₃ composition containing ferric ions
31 of the invention removes more of the zinc coating than
32 a conventional HNO₃ solution. This is important
33 because less zinc is introduced to the plating
34 solution.

COMPARATIVE EXAMPLE IVA AND EXAMPLE IVB

IVA. This Example demonstrates that less zinc is deposited on the substrate to be metal plated when using the double zincate method of the invention as compared to the conventional zincate process.

CZ-46 aluminium alloy disks were treated using steps (1) - (4) of the procedure of COMPARATIVE EXAMPLE I. One group of the disks were randomly selected and immersed in a conventional, prior art, HNO_3 solution (50% by volume) for 1 minute at room temperature.

IVB. The other group of disks were immersed in a 50% by volume HNO_3 solution containing 0.5 g/l ferric ions, according to the present invention (supplied as ferric chloride) for the same length of time and temperature.

Both groups of disks were then immersed in a second zincate bath (as in step (6) of COMPARATIVE EXAMPLE I) for either 10, 20, 30, 40, 50 or 60 seconds at room temperature. The zincated disks were then stripped in 50% by volume HNO_3 and the amount of zinc deposited on the disk determined by Atomic Absorbance Spectrophotography.

FIGURE 4 shows that less zinc was deposited on the disks when using the method of the invention as compared to the conventional double zincate method. This is important because there is less surface disturbance and consequently a thinner, but denser coating of zinc is obtained. The iron apparently acts as an inhibitor thus retarding and thereby controlling

1 the dissolution of aluminium by zinc. Furthermore, the
2 thinner deposits of zinc will not contaminate the
3 subsequent electroless nickel bath as rapidly.

4

5 COMPARATIVE EXAMPLE VA AND EXAMPLE VB

6

7 VA. Alumium 5586 alloy disks were plated using the
8 procedure of COMPARATIVE EXAMPLE I to a thickness of
9 about 0.40 mils. All the tests were run under the same
10 plating conditions of 84°C, pH 4.6, a work load of 0.31
11 ft²/gal, continuous filtration and plating time of
12 2 hours. The nickel, pH and sodium hypophosphite were
13 continuously replenished over the 2 hour plating time
14 using an automatic controller.

15

16 FIGURE 5A represents the nickel surface resulting from
17 using the above conventional zincating and plating
18 procedure.

19

20 VB. FIGURE 5B represents the nickel surface resulting
21 from using the above procedure with the exception that
22 0.5 g/l ferric ions (as ferric chloride) were added to
23 the nitric acid (step (5)).

24

25 FIGURE 5C represents the nickel surface resulting from
26 the above procedure with the exception that 0.75 mg/l
27 cadmium was added to the nickel plating bath before
28 plating and not replenished during the 2 hour plating
29 time.

30

31 FIGURE 5D represents the nickel surface resulting from
32 using the above procedure with the exception that 0.5
33 g/l ferric ions (as ferric chloride) were added to the

1 nitric acid (step 5) and 0.75 mg/l cadmium was added to
2 the nickel plating bath and not replenished during the
3 two hour plating time.

4
5 As can clearly be seen from the figures, the
6 conventional process produces a rough surface having
7 many nodules. Figures 5B and 5C show the beneficial
8 effects of using ferric ions and cadmium, respectively
9 and Figure 5D shows the extremely smooth surface
10 provided using the preferred method of the invention.

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CLAIMS

1. A method of forming a metal coating on an aluminium substrate, the method comprising:

(a) forming a zinc or zinc alloy deposit on the substrate;

(b) contacting the substrate with a zinc removing composition containing a source of Group VIII metal ions; and

(c) optionally repeating (a).

2. A method as claimed in claim 1 wherein (c) is not optional.

3. A method as claimed in claim 1 or 2 wherein in (a) and/or (c) the zinc or zinc alloy is formed by contacting the substrate with a zinc or zinc alloy plating composition.

4. A method as claimed in claim 3 wherein the plating composition suitably comprises a source of zinc ions, an alkali and optionally a source of metal alloy ions.

5. A method as claimed in any of claims 1 to 4 wherein the zinc removing composition contains nitric acid.

6. A method as claimed in any of claims 1 to 5 where the Group VIII metal is iron, cobalt or nickel.



- 1 7. A method as claimed in any of claims 1 to 6
2 wherein the Group VIII metal ion is a ferric ion.
3
- 4 8. A method as claimed in any of claims 1 to 7
5 wherein the Group VIII metal ion is provided in an
6 amount of from 0.1 to 1.0 g/l.
7
- 8 9. A method as claimed in any of claims 1 to 8
9 wherein the zinc removing composition comprises 50% by
10 volume nitric acid.
11
- 12 10. A method as claimed in any of claims 3 to 9
13 wherein the plating composition contains an hydroxide.
14
- 15 11. A method as claimed in claim 10 wherein the
16 hydroxide is an alkali metal hydroxide.
17
- 18 12. A method as claimed in any of claims 3 to 11
19 wherein the plating composition contains an anionic
20 wetting agent.
21
- 22 13. A method as claimed in any of claims 1 to 11
23 comprising:
24
- 25 (a) optionally cleaning an aluminium substrate
26 with a non-etch cleaner;
27
- 28 (b) optionally etching the aluminium substrate;
29
- 30 (c) optionally de-smutting the aluminium
31 substrate;
32
33



* C L M S *

- 1 (d) forming a zinc or zinc alloy deposit on the
2 aluminium substrate;
3
- 4 (e) contacting the aluminium substrate with a
5 zinc removing composition containing nitric
6 acid and a source of Group VIII metal ions;
7
- 8 (f) forming a zinc or zinc alloy deposit on the
9 aluminium substrate;
10
- 11 (g) forming a metal coating other than zinc on
12 the aluminium substrate by electroless
13 plating using a metal plating composition
14 comprising a source of metal ions, a source
15 of cadmium ions and a reducing agent; and
16
- 17 (h) optionally repeating (g) to provide a
18 different metal coating.
19
- 20 14. A method as claimed in claim 13 wherein the
21 non-etch cleaner is alkaline.
22
- 23 15. A method as claimed in claim 13 or 14 wherein the
24 non-etch cleaner is a non-silicated alkaline cleaner.
25
- 26 16. A method as claimed in any of claims 13 to 15
27 wherein the etchant is acidic.
28
- 29 17. A method as claimed in any of claims 13 to 17
30 wherein the de-smutting agent contains nitric acid
31 and/or sulphuric acid and optionally a fluoride salt.
32
- 33 18. A method as claimed in any of claims 13 to 17



1 wherein (a), (b), (c) and (h) are not optional.

2

3 19. A method as claimed in any of claims 13 to 18,
4 wherein in (g) the cadmium is provided at a level of
5 from 0.1 to 1.0 mg/l.

6

7 20. An aluminium substrate having a metal coating
8 prepared according to a method as claimed in any of
9 claims 1 to 19.

10

11 21. An aluminium substrate having a metal coating
12 formed according to a method substantially as herein
13 described with reference to any of the Examples Ib,
14 IIb, IIIb, IVb or Vb.

15

16 22. A method of forming a metal coating on an
17 aluminium substrate substantially as herein described
18 with reference to the Examples Ib, IIb, IIIb, IVb or
19 Vb.

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