

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

**0 368 470
A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **89310173.3**(51) Int. Cl.⁵: **C25D 5/44, C25D 11/12**(22) Date of filing: **04.10.89**(30) Priority: **14.10.88 CA 580280**(43) Date of publication of application:
16.05.90 Bulletin 90/20(64) Designated Contracting States:
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London WC2A 1HZ(GB)(54) **Methods for depositing finish coatings on substrates of anodisable metals and the products thereof.**

(57) The invention provides a method of depositing a layer of a finish metal on substrates of anodisable metals which comprises the steps of

a) anodising the substrate at the said surface to produce a porous anodised layer of thickness from about 0.5 to about 50 micrometres and having pores therein of transverse dimension from about 0.005 to 0.10 micrometres;

b) depositing a pore-filling metal into the pores using AC or modified AC deposition to completely fill the pores with the metal up to the surface of the anodized layer, and continuing the deposition of the pore-filling metal to form a continuous support layer on the surface of the anodised layer of thickness in the range about 0.5 to 3 micrometres; and

c) depositing at least one coating of a finish metal on the support layer.

The method is particularly useful for plating finish coatings of chromium on aluminium and its alloys.

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METHODS FOR DEPOSITING FINISH COATINGS ON SUBSTRATES OF ANODISABLE METALS AND THE PRODUCTS THEREOF

Field of the Invention

This invention is concerned with improvements in or relating to methods for depositing finish coatings on substrates of anodisable metals, such as aluminum and its anodisable alloys, and to the products of such methods, and especially but not exclusively to methods for plating finish coatings of chromium on aluminum and its alloys.

Review of the Prior Art

The deposition of chromium and other metals suitable as "finish" coatings on a substrate, usually steel or aluminum, is a well-developed art. Plating on less easily oxidized metals such as steel is relatively routine, involving for example the deposition of a layer of copper directly on the steel substrate, followed in succession by a thick "semi-bright" nickel layer, a thinner "bright" nickel layer, and an even thinner finish layer of the chromium; the chromium is semi-transparent and the bright appearance is actually provided by the bright nickel layer seen through the finish chromium layer.

Plating on anodisable metals, such as aluminum and its anodisable alloys, is considerably more difficult owing to their relative ease of oxidation, and the consequent inevitable presence of an oxide coating which must be removed if adequate adhesion of the deposited layers to the underlying metal substrate is to be obtained. The art currently is dominated by two methods of preparing the substrate surface, namely zincate and stannate immersion. In these processes the substrate surface is immersed in a suitable zincate or stannate solution, usually of the sodium salt, together with other additions that have been found in practice to increase the appearance and adhesion of the coatings. The zinc or tin atoms respectively displace aluminum atoms at the surface, in the process removing the oxide layer, to result in an adherent zinc or tin layer on which other layers, for example copper followed by nickel, can be deposited to constitute the finish layer, or to constitute a support layer receiving a finish layer, e.g. of chromium. Both of these processes are relatively expensive and are therefore mainly used on expensive commodities. The stannate immersion processes are reported to provide better anti-corrosion performance and adhesion of the resultant coatings, but are the more expensive of the two because of the more expensive components and longer process-

ing time.

It has also been proposed to deposit adherent metal coatings directly on aluminum or aluminium alloy substrates by producing a porous anodized layer at the surface of the substrate onto which the subsequent metal layers are deposited; this anodized layer incorporating the oxide layer that was present on the substrate surface. In an article entitled "Plating on Aluminum, a Review" by D.S. Lashmore, published in the June 1985 issue of "Plating & Surface Finishing" (pp 36-39), summarizing previous publications, it was reported that studies have shown that there must be a minimum pore size in the anodized coating, into which the subsequent coatings can mechanically "lock" or "key", and that this limits the process to the use of electrolytes that will produce fairly large pores of the order of 0.07 micrometres (700 Angstroms). The report goes on to state it has been found empirically that only anodising solutions comprising phosphoric acid are successful, sulfuric or oxalic acid sometimes being mixed with the phosphoric acid. The report further states that the adhesion of the subsequent coatings is primarily mechanical, with the cohesive strength of the porous oxide coatings to the metal substrate being the limiting factor, so that improvements in the anodic process should be directed towards increasing this cohesive strength and the strength of the oxide layer itself. Lastly, it mentions that local turbulence, presumably in the anodizing bath, or changes in the electrochemical potential, can lead to branching of the pores, and these phenomenon lead to higher mechanical adhesion. Despite developments of these phosphoric acid anodizing/coating processes for over 50 years they have not yet been widely adopted commercially, apparently because of relatively poor adhesion and brightness.

There is disclosed in U.S. Patents Nos. 4,111,763 and 4,163,083 processes for plating chromium on aluminum and its alloys comprising anodizing the surface to be plated in an acid bath, impregnating the anodized layer with a chemical that is pyrolyzable to form an electronically conductive oxide, and then heating the surface to pyrolyse the chemical to form the oxide in the pores of the anodized layer, thereby providing an anodic coating of high ionic resistance forming a continuous high corrosion resistance barrier layer upon which the plating of successive metal layers can be continued. Suggested chemicals are stannous chloride and orthobutyl titanate to form respectively stannous oxide and conductive titanium oxide (Ti_2O_3); with titanium the surface can be further treated

after plating of the finish coating to convert the (Ti_2O_3) to insulating titanium dioxide (TiO_2).

Definition of the Invention

It is therefore the principal object of the present invention to provide new methods for plating metal layers on substrates of aluminum and its alloys.

In accordance with the present invention there is provided a new method of depositing a layer of a finish metal on a surface of a substrate of an anodisable metal, the method including the steps of:

a) anodising the substrate at the said surface to produce a porous anodised layer of thickness from about 0.5 to about 50 micrometres and having pores therein of transverse dimension from about 0.005 to 0.10 micrometres;

b) depositing a pore-filling metal into the pores using AC or modified AC deposition to completely fill the pores with the metal up to the surface of the anodised layer, and continuing the deposition of the pore-filling metal to form a continuous support layer on the surface of the anodised layer of thickness in the range about 0.5 to 3 micrometres; and

c) depositing at least one coating of a finish metal on the support layer.

Also in accordance with the invention there is provided a new method of depositing a layer of a finish metal on a surface of a substrate of an anodizable metal, the method including the steps of:

a) anodizing the substrate at the said surface to produce a porous anodized layer, the substrate surface first being anodized to produce a large-pore anodised layer portion with large pores opening to its free surface, and subsequently being anodised to produce a small-pore anodized layer portion between the large-pore layer portion and the remainder of the substrate communicating with the large pores of the large-pore layer portion.

b) depositing a pore-filling metal on to the porous anodised layer to fill the pores therein and to form a support layer of the pore-filling metal thereover; and

c) depositing at least one layer of a finish metal on the support layer.

Description of the Drawings

Methods of depositing various layers of metals on a surface of an anodisable substrate, and the products of such methods, constituting particular preferred embodiments of the invention, will now be described by way of example with reference to

the accompanying drawings, wherein:-

Figure 1 is a cross-section through the surface and adjacent portion of an aluminum substrate and through a porous anodised layer that has been formed thereon by sulfuric acid anodising;

Figure 2 is a cross-section similar to Figure 1 through a porous anodised layer that has been formed on the anodisation substrate by phosphoric acid anodising;

Figure 3 is a cross-section through the surface and adjacent portion of an aluminum substrate, through the porous anodised layer formed in accordance with the invention, and through the various layers of metal that have been deposited on the anodised layer;

Figure 4 is a cross-section to a much enlarged scale of the small portion 4 of Figure 3, showing the anodised layer and the immediately adjacent metal layers; and

Figure 5 is the same cross-section as that of Figure 4, showing a part thereof to a still larger scale;

Description of the Preferred Embodiments

The acid most widely used for porous anodising is sulfuric acid because of its ready availability and lower cost, although phosphoric, oxalic and chromic acids, and mixtures of these and other acids, can also be used. The anodised layer is inherently porous in structure because of the manner of its formation, and a typical structure of a layer 10 obtained by sulfuric acid anodising of an aluminum substrate 12 is shown in Figure 1. For convenience in drawing the surfaces of the layers are shown as flat, but in practice, even at quite low magnification these surfaces will be seen to be highly irregular.

Figure 1 shows an anodised layer 10 of aluminum oxide (Al_2O_3) of about 5 micrometres (50,000 Angstroms) thickness, that typically will be produced using sulfuric acid at about 20° C and of about 165g/litre or 15% by weight concentration, employing an anodising voltage of about 15-20 volts for 10 minutes. The porous structure obtained is relatively uniform, although highly idealised as shown in Figure 1 for convenience in drawing, and typically the pores will be found to average 0.015 micrometres (150 Angstroms) in transverse dimension, spaced on average about 0.024 micrometres (240 Angstroms) from one another. The pores do not end at the surface of the aluminum substrate, but instead they are on average spaced about 0.015 micrometres (150 Angstroms) from that surface to form a continuous non-porous barrier layer of the relatively non-conductive aluminum oxide, the thickness of this layer depending principally

directly on the value of the anodising voltage. Usually with sulfuric acid anodising this thickness averages about 0.0010 to 0.0014 micrometres (10 to 14 Angstroms) per volt. It may be noted that references herein and in the literature to pore sizes, etc. are usually made in Angstroms, while references to thicknesses are made in micrometres, merely to avoid the need to refer to small fractions, 1 micrometre being equal to 10,000 Angstroms.

It has been found possible in previous commercial practice to form coatings of deposited metal that are sufficiently strong and stable of up to about 5 micrometres thickness, but beyond this value the hydrogen that is generated in the long, narrow pores (i.e. length to width ratio in the sample illustrated of about 330:1) tends to cause spalling of the coating, destroying its strength to the extent that it is unsuitable to receive and retain the subsequent metal layers. Another problem is that it is difficult to deposit a sufficiently adherent coating of a pore-filling metal into the long narrow pores employing conventional D.C. plating methods. Thus, there is too great a tendency for the plating step to cause physical disruption of the anodised layer, so that the plated metal layer is poorly adherent.

Figure 2 shows an anodised layer 10 of aluminum oxide (Al_2O_3) of about 2 micrometres (20,000 Angstroms) thickness that typically will be produced using phosphoric acid at about 20°C and of about 100g/litre or 10% by weight concentration, employing an anodising voltage of about 50-60 volts for 10 minutes. The pores themselves are of much larger transverse dimension to give a much lower length/width ratio (20:1 in this example), and they are much more widely spaced apart at an average value of about 0.07 micrometres (700 Angstroms). The barrier layer is thicker because of the higher voltage used; e.g. 60 volts gives a layer of about 700 Angstroms thickness. Such much larger pores are easier to plate into using DC current, but despite considerable work on this type of anodising, to the best of our knowledge it has not been adopted commercially to any great extent, if at all, because of this adhesion problem, and also because of poor appearance of the resultant coatings.

Figure 3 is a cross-section through an aluminum substrate 12 at the surface of which there has been formed an anodised layer 10 of aluminum oxide in accordance with this invention, a portion 4 of which is shown to a larger scale in Figure 4. A pore-filling metal, semi-bright nickel in this embodiment, is deposited on the anodised layer to form a support layer 14, and then a layer 15 is deposited to the desired thickness, which again in this embodiment is semi-bright nickel. This semi-bright nickel layer 15 is followed by a layer 16 of bright nickel and a thin finish layer 18 of chromium.

Referring now to Figures 4 and 5, the layer 10 is formed by means of a first anodising step at the surface of the substrate 12 to produce a first layer portion having relatively large transverse dimension pores 20 which open to the substrate free surface. This first step is stopped when the corresponding layer portion is sufficiently thick, and a second anodising step is then employed to produce a second layer portion having relatively small transverse dimension pores 22 that open into the large pores 20, the barrier layer 24 being formed between this second layer portion and the substrate 12. In the embodiment illustrated by Figures 4 and 5 the pores 20 are of 0.09 micrometre (900 Angstroms) transverse dimension and about 1.5 micrometres (15,000 Angstroms) depth, being spaced about 0.07 micrometre (700 Angstroms) from one another while the small pores 22 of the second layer communicating with the large pores 20 are of 0.015 micrometre (150 Angstroms) transverse dimension and about 2.5 micrometres (25,000 Angstroms) depth, being spaced about 0.024 micrometre (240 Angstroms) from one another. Such a composite structure can be filled with the metal of the layer 14 without disruption of the pores and/or of the barrier layer, while providing the necessary good adhesion between the layers 10 and 14, and also the necessary strength of the layer.

The preferred method of depositing the pore-filling metal of the layer 14 into the composite pores 20 and 22 without damage to the barrier layer is by use of one of the known systems employing what is referred to herein and in the appended claims as a modified A.C. current, preferably one in which a predetermined negative-going D.C. current has been superimposed on the A.C. current. Such a system avoids the disruption of the barrier layer that would be produced by a pure D.C. current. It may be noted however that owing to the rectification characteristic of the aluminum oxide an A.C. current alone will produce deposition of the metal and production of a support layer sufficient for relatively thin anodic coatings e.g. 2 micrometres. For thicker coatings such unmodified A.C. deposition gives insufficient pore penetration and at too slow a deposition rate to produce the support layer. The rate and thickness are therefore increased by increasing the D.C. component to the maximum level that does not cause disruption. This method of deposition is disclosed for example in U.S. Patent No. 4,226,680, issued to Alcan Research and Development Limited, the disclosure of which is incorporated herein by this reference. Other "modified A.C." systems are also possible. For example, the superimposed D.C. component is commonly produced by means of a negative bias, which is increased as necessary, while the equivalent effect can be obtained by

reduction of positive bias. Another system offsets the A.C. waveform in a manner that will produce an effective negative bias. A further way is to increase the amplitude of the negative portion of the waveform relative to that of the positive portion, which again has the same effect.

In a preferred process the substrate is first phosphoric acid anodised with the anodising voltage starting in the usual higher range of values for phosphoric acid, and is decreased during this step until at the end of the phosphoric acid anodising it has reached the range of lower values suitable for sulfuric acid anodising, when the electrolyte is changed, usually by moving the article from the phosphoric acid bath to the sulfuric acid bath, with thorough water rinsing in between, thereby avoiding the sudden application of electric potentials that may deleteriously affect the coating.

The use of an anodic film before plating introduces the possibility, if desired, of a reduction in the thickness of the subsequent plated layers with consequent cost savings. Further reductions are possible by using a thicker and/or stronger anodic film such as that produced using low temperature sulfuric acid anodising. It will be understood that this industry is particularly cost conscious, especially with regard to the relatively expensive corrosion-resistant metals that are employed in the intermediate and finish coatings, so that any saving that can be achieved in their thickness for an equivalent performance in protection and/or appearance is commercially important.

In the processes of the invention the anodised layer 10 can be of thickness in the range 0.5 - 50 micrometres, usually in the range 1-10 micrometres, preferably in the range 2-6 micrometres, and more preferably 3-5 micrometres, with a thickness of 5 micrometres being usually commercially suitable. The pore-filling material need not form a support coating of more than about 2 micrometres thickness and excellent results can be obtained with the application of a single thin finish coating of chromium over the pore-filling metal layer. The preferred pore-filling metal is nickel. Metals other than nickel, such as cobalt, tin or copper, can also be used. Because of the thin coatings that are employed it is preferred in some processes to pre-treat the surface of the anodisable metal to obtain a very smooth surface; this can be a "macro" treatment by buffing and/or a "micro" treatment of chemical or electro-brightening. The support layer of the pore-filling metal preferably is of thickness in the range 0.5 - 3 micrometres, and more preferably in the range 1-2 micrometres. The chromium layer preferably is of thickness in the range of 2-3 micrometres.

The anodising processes described employing acid baths in the temperature range 20-35°C are

usually characterised as "conventional" anodising, but "hard" anodising processes can also be employed for the invention, the usual bath temperature being in the range 3-7°C. Such hard anodised layers are usually thicker than the conventional anodised layers. Such hard layers are also the basis for the pore-filling metal deposition of nickel or cobalt, which can be the support layer for further deposits, which further deposits can be thinner than those normally previously used.

Another aspect of the present invention provides deposition processes in which a single stage sulfuric acid anodisation of the surface of an anodisable substrate is followed by a step in which the pores are completely filled with pore-filling metal using an A.C. with superimposed D.C. or other modified A.C. deposition current, and the deposition is continued until there is a layer of the pore-filling metal of only about 2 micrometres on the surface of the anodised layer. Prior processes have been disclosed for example, as in the above-mentioned U.S. Patent No. 4,226,680, and also U.S. Patent No. 4,251,330, the disclosure of which is also incorporated herein by this reference, in which sulfuric acid anodising is followed by only partial filling of the pores with metal to produce a desired colour.

Example 1

In a specific example of a process of the invention the aluminum substrate is pretreated, usually by cleaning with appropriate alkaline and/or acid solutions, and is then anodised using 10% concentration by weight of phosphoric acid at 21°C. The voltage is held at 60 VDC for 2 minutes then decreased progressively to 15 VDC over a period of 3 minutes and held at 15 VDC for 2 minutes. The article is then rinsed in water and moved to a sulfuric acid anodising bath with 15% by weight concentration acid at 21°C and held at 15 VDC for 5 minutes. Nickel is then deposited in the pores using a Watts nickel bath employing for example 240 g/L nickel sulphate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$), 60 g/L nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) and 45 g/L of boric acid (H_3BO_3), the bath being held at a pH of 4.5 and temperature of 21°C. The bath is employed with AC current taking 1 minute to increase the voltage to 12 1/2 VAC; the voltage is then held at 12 1/2 VAC for 2 minutes and subsequently is held for 8 minutes at 12 1/2 VAC with a -2 VDC bias to provide the main deposition current. Further nickel and chromium layers are then deposited using any suitable conventional processes.

In other processes the temperature of the phosphoric acid electrolyte can be in the range 21°C - 35°C, and the time for increase to 60 VDC

can be in the range 2-5 minutes.

Example 2

A substrate of mechanically buffed aluminum of type AA6463, as commonly used for architectural application, is pretreated in appropriate alkaline and acid cleaning solutions, and is then anodised using 10% by weight phosphoric acid at 21 °C; the voltage is held at 60VDC for 2 minutes then decreased progressively to 15VDC over a period of 3 minutes and held at 15VDC for 2 minutes. The article is then rinsed in water and moved to a 15% by weight sulphuric acid bath at 21 °C and held at 15VDC for 5 minutes. A support layer of nickel is deposited using the bath of example 9 below and the electrical protocol of example 10 below; thereafter a 25 micrometres thick layer of electroless nickel is applied, using a process as suggested for example 5.

Example 3

A substrate of mechanically buffed aluminum alloy of type AA7029, as commonly used for automotive bumpers, is pretreated and anodised as in example 2. A support layer of nickel is deposited as in example 10 below followed by a 40 micrometres thick layer of semi-bright nickel, a 15 micrometre thick layer of bright nickel, and a 2 micrometre thick layer of chromium, all applied using conventional plating techniques. The resulting product has a bright "chromium" finish, as is desired for such an automotive application.

Example 4

A substrate of mechanically buffed aluminum of type AA6063, which is a non-bright material as commonly used for non-decorative architectural purposes, is pretreated and anodised as in example 2. A support layer of nickel is deposited as in example 10, followed by a 15 micrometre thick layer of bright nickel and a 2 micrometre thick layer of chromium, applied using conventional plating techniques. The resulting product had a bright "chromium" finish.

Example 5

The production of the porous anodised layer 10 with a pore-filling metal and a support layer as described in Example 1, is followed by electroless deposition, the metal being selected from nickel,

cobalt and copper. There are a large number of electroless compositions suitable for this purpose as disclosed for example in an article by N. Feldstein in Metal Finishing, 51st Guidebook and Directory Issue, 1983, Vol. 81, No. 1A entitled Electroless (Autocatalytic) Plating (pp 468-476), the disclosure of which is incorporated herein by this reference. Because of the additional strength and adherence of the anodised layer the electroless layer can be made much thicker than the support layer, up to about 25 micrometres, to result in a mirror-bright finish suitable for decorative application.

Example 6

A substrate of mechanically buffed aluminum of type AA6061, which is an extruded material for general application, such as machine stock, is pretreated in appropriate alkaline and acid cleaning solutions. It is then anodised using 10% byweight phosphoric acid at 21 °C, the voltage being held at 60 VDC for 2 minutes then decreased progressively to 20 VDC over a period of 3 minutes and held at 20 VDC for 2 minutes. The article is then rinsed in water and hard anodised by moving to a 15% by weight sulphuric acid bath at 5 °C and held at 20 VDC for 5 minutes. A support layer of nickel and a 25 micrometre layer of electroless nickel are added as in examples 2 and 5. The resulting product has a "stainless steel" appearance combined with good abrasion resistance, making it very suitable for engineering applications requiring a hard surface

Example 7

An aluminum substrate is pretreated and then anodised using a 15% concentration bath of sulfuric acid at 21 °C and for 10 minutes at 15 VDC, producing an anodised layer of about 5 micrometres thickness. This is then plated using either the Watts nickel plating bath of example 1 or a cobalt plating bath, for example one consisting of 100 g/L of cobalt sulfate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$), 40 g/L of boric acid (H_3BO_3), and 150 g/L of magnesium sulfate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), the pH being 4.4 and the bath being operated at 16 °C

Example 8

A substrate of bright rolled aluminum of type AA5657, as used commercially for bright automotive trim is pretreated in appropriate alkaline and acid cleaning solutions, followed by chemical

brightening in a phosphoric acid based solution. It is then anodised to result in a porous anodised layer of 2 micrometres thickness using sulphuric acid of 15% by weight (165g/L) at 20°C, and employing a voltage of 15VDC for 4 1/2 minutes. After thorough rinsing, cobalt is deposited into the pores using the electrolyte of example 6 with A.C. current applied at 12 1/2 VAC for 5 minutes. A thin chromium layer of 2 micrometres is then applied using conventional plating techniques. The resulting product had the appearance typical of stainless steel.

Example 9

A substrate of bright rolled aluminum of type AA5252, also used commercially for bright automotive trim is bright anodised to a thickness of 2 micrometres, as described in example 8. After thorough rinsing, nickel is deposited into the pores using the same electrical parameters as in example 8 and using a Watt's nickel bath of 240g/L nickel sulphate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$), 60g/L nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) and 45g/L boric acid (H_3BO_3) the bath being held at a pH of 4.5 and temperature of 21°C. A thin chromium layer of 2 micrometres thickness is then applied using conventional plating techniques. The resulting product had the appearance typical of stainless steel.

Example 10

A substrate of mechanically buffed extruded aluminum of type AA6463, as commonly used for architectural applications, is bright anodised to a thickness of 5 micrometres as described in example 7 for 10 minutes. After thorough rinsing nickel is deposited into the pores using a Watt's nickel bath as described in example 8. A.C. current is used by ramping over a period 1 minute to 12 1/2 VAC, held at this voltage for 2 minutes then a negative 2 VDC shift is superimposed on the A.C. for a further 8 minutes. A layer of 5 micrometres thickness of electroless nickel is then applied using a conventional electroless plating technique. The resulting product had the appearance characteristic of polished stainless steel.

Example 11

A substrate of bright rolled aluminum of type AA5657 is bright anodised to a thickness of 5 micrometres as described in example 8 for 10 minutes. After thorough rinsing nickel is deposited into the pores using a Watt's nickel bath as de-

scribed in example 9. The A.C. voltage is set initially at 12 1/2 VAC with a negative 2 VDC bias and the current is ramped up to this level over a period of 1 minute and maintained at this level for 10 minutes. A layer of 5 micrometres thickness of electroless nickel is then applied using a conventional electroless plating technique. The resulting product had the same appearance as with example 10.

The processes of the invention are not limited to the production of architectural, automotive and decorative finishes, and an example of an alternative application is the deposition of a black chrome finish layer on a nickel support layer for solar selective absorber applications. A similar process can be employed for the production of magnetic discs, also involving the production of a support layer of nickel followed by a chromium layer.

Claims

1. A method of depositing a layer of a finish metal on a surface of a substrate of an anodisable metal, characterized by the steps of:

a) anodising the substrate at the said surface to produce a porous anodised layer of thickness from about 0.5 to about 50 micrometres and having pores therein of transverse dimension from about 0.005 to 0.10 micrometres;

b) depositing a pore-filling metal into the pores using AC or modified AC deposition to completely fill the pores with the metal up to the surface of the anodized layer, and continuing the deposition of the pore-filling metal to form a continuous support layer on the surface of the anodised layer of thickness in the range about 0.5 to 3 micrometres; and

c) depositing at least one coating of a finish metal on the support layer.

2. A method as claimed in claim 1, characterized in that the anodisable metal is selected from aluminum and anodisable alloys thereof.

3. A method as claimed in claims 1 or 2, characterized in that the pore-filling metal is selected from nickel, cobalt, copper, tin and mixtures thereof.

4. A method as claimed in any one of claims 1 to 3, characterized in that the finish metal is chromium.

5. A method as claimed in any one of claims 1 to 3, characterized in that the layer of chromium finish metal is of thickness about 1-5 micrometres.

6. A method as claimed in any one of claims 1 to 3, characterized in that the finish metal is electroless plated on the support layer.

7. A method as claimed in any one of claims 1 to 3, characterized in that the finish metal is elec-

troless plated to a thickness of about 10-25 micrometres on the support layer.

8. A method as claimed in any one of claims 1 to 3, characterized in that the finish metal is electroless plated nickel to a thickness of about 10-25 micrometres on the support layer.

9. A method as claimed in any one of claims 1 to 8, characterized in that the substrate is first anodized at the surface to produce a large-pore anodised layer portion with large pores opening to its free surface, and is subsequently anodised to produce a small-pore anodised layer portion between the large-pore layer portion and the remainder of the substrate with the small pores of the small-pore layer portion in communication with the large pores of the large-pore layer portion.

10. A method as claimed in claim 9, characterized in that the first anodising to produce large pores is acid anodising using phosphoric acid and the subsequent anodising to produce small pores is acid anodising using sulfuric acid, or chromic acid or oxalic acid, or mixtures thereof.

11. A method as claimed in claim 9, characterized in that the substrate is first phosphoric acid anodised to produce the large-pore anodised layer portion, and is subsequently sulfuric acid anodised to produce the small-pore anodised layer portion.

12. A method as claimed in claim 9, characterized in that the substrate surface is first anodised to produce a large-pore anodised layer portion with large pores of transverse dimension from about 0.07 to 0.1 micrometre, and is subsequently anodised to produce a small-pore anodised layer portion with small pores of corresponding transverse dimension from about 0.01 to 0.02 micrometre.

13. A method as claimed in claim 9, characterized in that the substrate surface is first anodised to produce a large-pore anodised layer portion with large pores of transverse dimension of about 0.09 micrometre, and is subsequently anodised to produce a small-pore anodised layer portion with small pores of corresponding transverse dimension of about 0.015 micrometre.

14. A method as claimed in any one of claims 9 to 14, characterized in that the substrate is first phosphoric acid anodised while the anodising voltage is increased from a value for sulfuric acid anodising to a maximum value for phosphoric acid anodising, and subsequently is reduced to the said value for sulfuric acid anodising, and thereafter is sulfuric acid anodised while the anodising voltage is held at the value for sulfuric acid anodising.

15. A method of depositing a layer of a finish metal on a surface of a substrate of an anodizable metal, the method including the steps of:

a) anodizing the substrate at the said surface to produce a porous anodized layer, the substrate

surface first being anodized to produce a large-pore anodised layer portion with large pores opening to its free surface, and subsequently being anodised to produce a small-pore anodised layer portion between the large-pore layer portion and the remainder of the substrate communicating with the large pores of the large-pore layer portion;

b) depositing a pore-filling metal on to the porous anodised layer to fill the pores therein and to form a support layer of the pore-filling metal thereover; and

c) depositing at least one layer of a finish metal on the support layer.

16. A method as claimed in claim 15, characterized in that the first anodising to produce large pores is acid anodising using phosphoric acid and the subsequent anodising to produce small pores is acid anodising using sulfuric acid, or chromic acid or oxalic acid, or mixtures thereof.

17. A method as claimed in claim 15, characterized in that the substrate is first phosphoric acid anodised to produce the large-pore anodised layer portion, and is subsequently sulfuric acid anodised to produce the small-pore anodised layer portion.

18. A method as claimed in claim 15, characterized in that the substrate surface is first anodised to produce a large-pore anodised layer portion with large pores of transverse dimension from about 0.07 to 0.1 micrometre, and is subsequently anodised to produce a small-pore anodised layer portion with small pores of corresponding transverse dimension from about 0.01 to 0.02 micrometre.

19. A method as claimed in claim 15, characterized in that the substrate surface is first anodised to produce a large-pore anodised layer portion with large pores of transverse dimension of about 0.09 micrometre, and subsequently is anodised to produce a small-pore anodised layer portion with small pores of corresponding transverse dimension of about 0.015 micrometre.

20. A method as claimed in any one of claims 15 to 19, characterized in that the substrate is first phosphoric acid anodised while the anodising voltage is increased from a value for sulfuric acid anodising to a maximum value for phosphoric acid anodising, and subsequently is reduced to the said value for sulfuric acid anodising, and thereafter is sulfuric acid anodised while the anodising voltage is held at the value for sulfuric acid anodising.

21. A method as claimed in any one of claims 15 to 20, characterized in that the anodised layer is of thickness from about 1 to 10 micrometres.

22. A method as claimed in any one of claims 15 to 21, characterized in that the support layer is of thickness from about 0.5 to 3 micrometres.

23. A method as claimed in any one of claims

15 to 22, characterized in that the finish layer is of thickness from about 1 to 5 micrometres.

24. A method as claimed in any one of claims 15 to 23, characterized in that the finish metal is electroless plated on the support layer.

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25. A method as claimed in any one of claims 15 to 23, characterized in that the finish metal is electroless plated to a thickness of about 10-25 micrometres on the support layer.

26. A method as claimed in any one of claims 15 to 23, characterized in that the finish metal is electroless plated nickel.

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27. A method as claimed in any one of claims 15 to 23, characterized in that the pore-filling metal is deposited using AC with superimposed DC deoposition to completely fill the pores and form the support layer.

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28. A substrate of anodisable metal having thereon a porous anodised layer, the pores of which are filled with pore-filling metal, a support layer of metal on the surface of the anodised layer, and a coating of a finish metal on the support layer, when prepared by a method as claimed in any one of claims 1 to 27.

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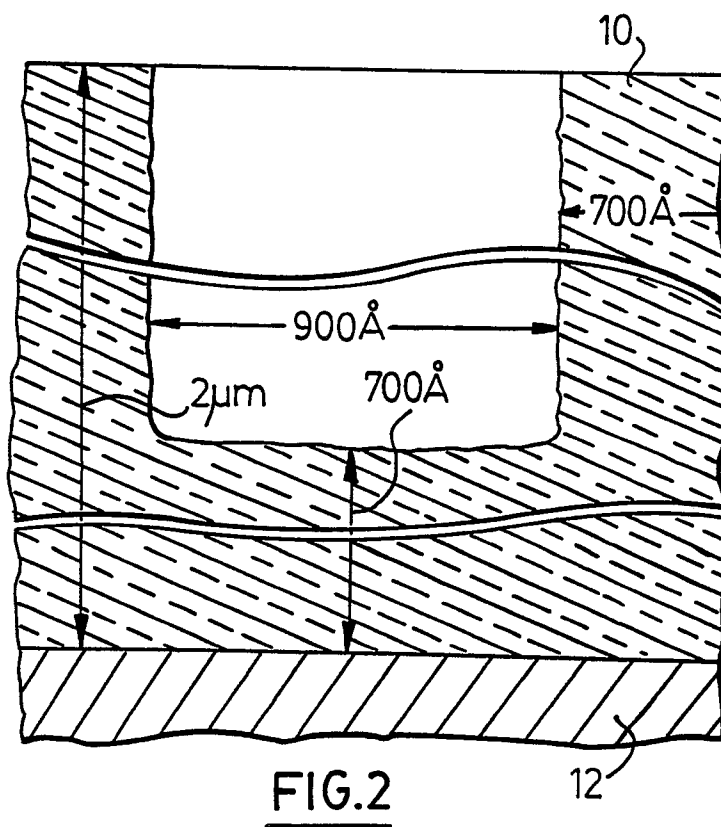
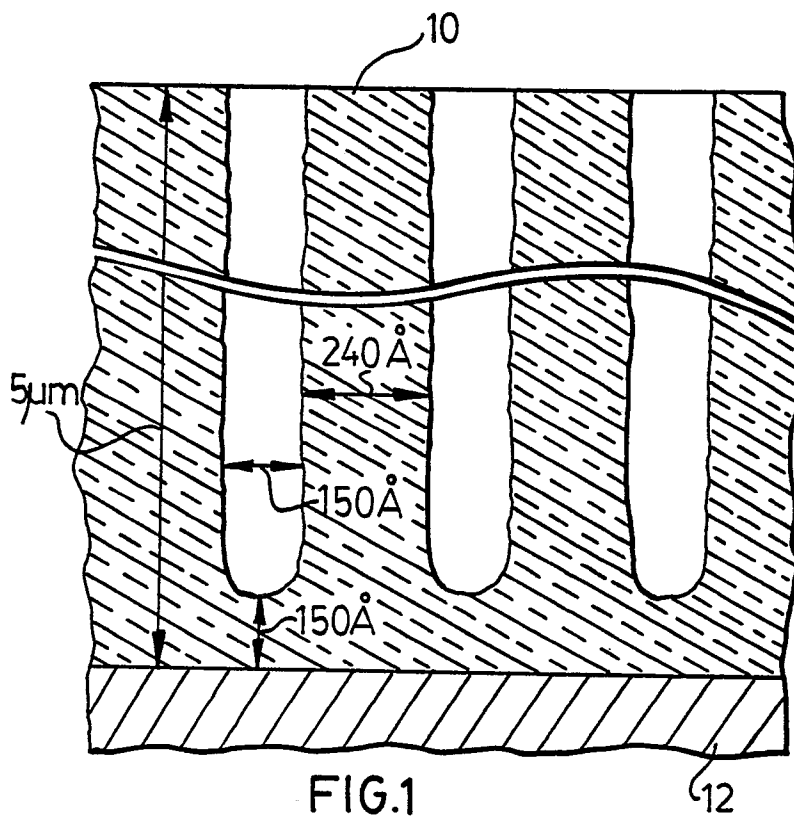
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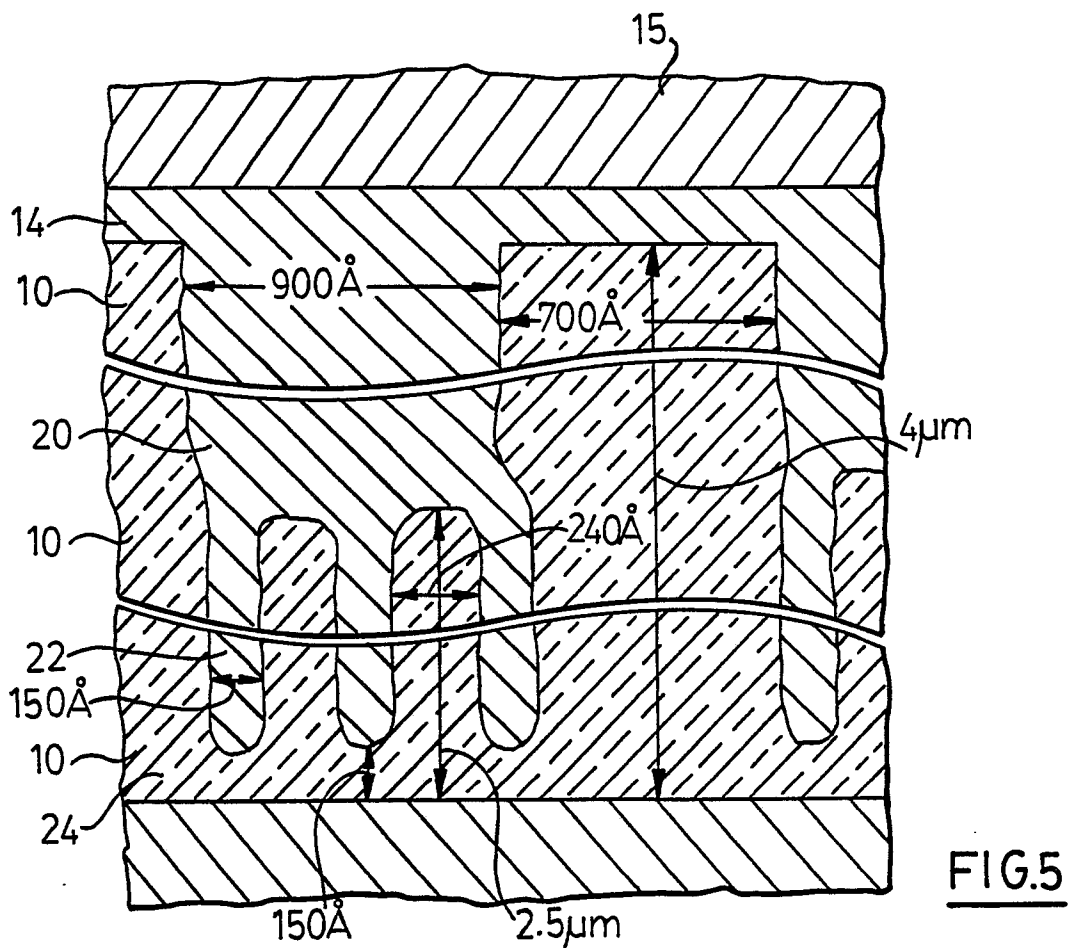
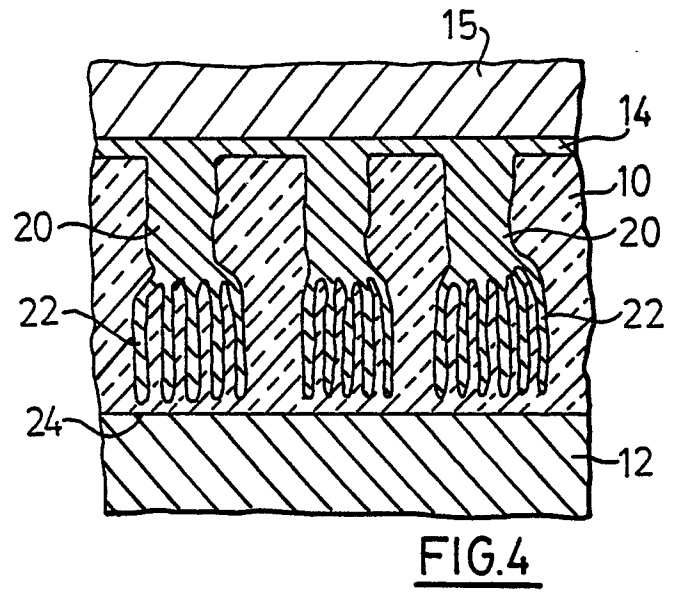
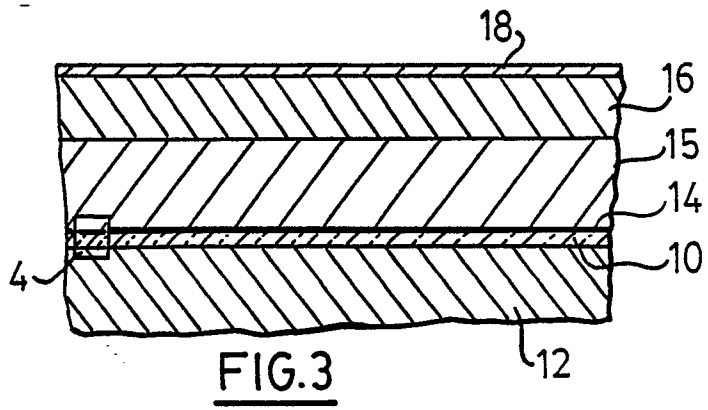
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 121 880 (HOECHST AG) ---		C 25 D 5/44
A	EP-A-0 178 831 (ALCAN INTERNATIONAL) ---		C 25 D 11/12
A,D	US-A-4 226 680 (ALCAN) ---		
A	S. WERNICK et al.: "The Surface Treatment and Finishing of Aluminium and its Alloys", vol. 2, Fifth Edition, 1986, pages 1011-1016 -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 25 D 5/44 C 25 D 11/04 C 25 D 11/12
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 16-01-1990	Examiner VAN LEEUWEN R.H.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	