

SEALING PROCEDURES FOR METAL AND/OR ANODISED METAL SUBSTRATES

TECHNICAL FIELD

5 The present invention relates to sealing procedures for metal and/or metal alloy substrates whether anodised or not but suitable in any event for anodised magnesium or magnesium alloy surfaces.

BACKGROUND OF THE INVENTION

10 Anodised films may commonly comprise a porous layer of metal oxide. If the pore structure did not exist, the anodic film could not form to a significant thickness owing to electrical resistance and the barrier to ionic transport posed by the oxide. While the pore structure allows a useful thickness of film to form, it may in some circumstances be a disadvantageous feature, as corrosive species may migrate through the pores to the underlying base metal.

15 Accordingly, it is often desirable to "seal" the pores. Such sealing implies an agent that either physically fills the pores and plugs them or an agent that reacts chemically with the oxide film causing a plug to form capping the pores.

20 In the case of aluminium, (a metal incidentally where an oxide layer provides some measure of protection inherently) a regular hexagonal pore structure forms as a result of anodisation in sulphuric acid solutions. This results as a consequence of the partial solubility of the forming oxide film in the electrolyte. However, the pores may be sealed very simply using boiling water or simple ionic salts at room temperature or intermediate temperatures. These cause a plug to form across the surface of each pore, sealing the coating.

25 Magnesium (a metal incidentally where an oxide layer does not provide inherent protection) does not feature a comparable pore structure to aluminium when anodised. Pore structures in anodic films on magnesium or magnesium alloy substrates are generally larger and not as well defined. Some anodisation processes result in highly irregular pore sizes and shapes as well as a broad distribution in both
30 size and shape. The pores do not usually result from solubility of the magnesium oxide in the electrolyte but from physical factors associated with the formation of the

film during electrochemical oxidation.

Simple solutions such as immersion of the anodised surface in boiling water or a simple ionic salt do not result in a sealed film.

Accordingly, a successful method of sealing anodised magnesium articles
5 requires the introduction of another species to physically plug the pores. Such a species must be inert and resistant to ingress of pitting initiators such as chloride ions, and of course, moisture as the presence of even small amounts of moisture may lead to galvanic corrosion and accelerated attack of the magnesium substrate.

The sealing agent must also be firmly bonded to the anodic film, preferably by
10 way of a chemical or strong physical bond and the seal, when applied must be chemically resistant.

While a number of methods may be employed to seal anodised films by way of providing a physical barrier to external agents, many of these are of low specification. Wet or dry paints, resins of various kinds and even oil may be used to
15 fill up the pores helping prevent corrosion from external agents. Generally these methods provide a modest increased resistance to corrosion but often these substances are too readily displaced from their sites within the pores. For some applications they may provide a satisfactory solution.

While it is an object of the present invention to provide procedures for sealing
20 anodised magnesium containing surfaces, preferably it or they also have application to other surfaces, eg; fabricated components of anodised magnesium alloy and aluminium.

BRIEF SUMMARY OF THE INVENTION

In a first aspect the present invention consists in a method of sealing the or a
25 surface of a material, an article, a component or an assembly (hereafter "article"), being an article having, at least in part, at least one of

- a metal surface,
- a metal alloy surface,
- an anodised metal surface, and
- 30 an anodised metal alloy surface,

said metal being an element selected from the group consisting of magnesium,

beryllium, titanium, zirconium, hafnium, zinc, and aluminium,

which method at least includes the steps of

- (I) if the article, at least in part, has said anodised surface(s), treating the anodised surface to a presence of a deactivating agent not substantially destructive of the anodised surface and/or

if the article, at least in part, has said non anodised metal or non anodised metal alloy surface(s), treating that surface type to a presence of a deactivating agent not substantially destructive of that surface, such deactivating agent(s) being

- (i) an acid or acids and/or
- (ii) a non-acid agent able to render the surface(s) both incapable of significant ionisation in the suspension and of reaction towards the suspension,
- (II) exposing the surface(s) to be sealed to a resin suspension whilst a voltage is caused to apply to such surface(s), the surface(s) being substantially free of surface activity (such as alkalinity or water soluble ions) prior to such exposure and the resin suspension being such as to be able to provide a coating on the surface(s) capable of subsequently curing on the surface(s) in curing conditions, and
- (III) subsequently allowing the cure and/or causing the cure of the coating on the surface(s) to provide the seal.

Preferably the resin suspension includes an aqueous phase and micelle formation is as a result of the dispersion of the resin in the water and the presence of reactive groups on the resin dissociate, with one ion going into the aqueous phase and the other staying with the resin. As a result a small charged micelle forms, the size of which depends on the charge, which in turn depends on the degree of dissociation which is dependent on the pH and conductivity of the aqueous phase.

Preferably the surface(s) after step (I) is substantially free of ionisable species (eg; alkalinity if metal is magnesium).

Preferably said metal element is selected from the group consisting of magnesium or aluminium or alloys thereof or fabricated mixed structures thereof.

Preferably the metal element is magnesium.

Preferably said deactivating agents are selected those (eg; including acid or acids) from those which form a sparingly soluble or insoluble magnesium salt. Some of the many agents which can be used with magnesium form the following salts:

- 5 Solubility of magnesium lactate = 33g/litre at 20°C
Solubility of magnesium tartrate = 8g/litre at 16°C
Solubility of magnesium fluoride = 0.076 g/litre at 18°C

of course the selection of deactivating agent is not restricted to these agents.

- Preferably said acid or acids is or are selected from the group consisting of
10 lactic acid, tartaric acid or hydrofluoric acid.

Preferably said resin suspension is one which upon curing will provide a polymer coating which, optionally, may include inclusions such as pigment(s), graphite, etc.

- Examples of polymers include polyurethanes, acrylics, polyacrylamelamines
15 and epoxies.

Preferably the resin suspension is one which includes water.

Preferably said polymer is a polyurethane and said resin suspension includes an isocyanate resin.

- Preferably said resin suspension includes water, a blocked isocyanate resin and
20 a source of -OH moieties selected from alcohols and glycols (eg; a glycol ether).

Preferably said subsequently allowing the cure and/or causing the cure of the coating on the surface(s) to provide the seal results from applying heat or a source of unblocking radiation to the coated surface(s).

Preferably the heating is to above 137°C.

- 25 Preferably the voltage caused to apply to such surface(s) is a cathodic voltage.

Preferably said cathodic voltage is applied in the form of a direct current with little or no alternating component.

In other forms said voltage caused to apply to such surface(s) is an anodic voltage provided the resin is configured to yield a negatively charged micelle.

- 30 Preferably the surface(s) is or are anodised, prior to such surface(s) being treated to a presence of a deactivating agent (eg; acid(s)).

Preferably the exposing of the surface(s) to the resin suspension is by means of dipping.

Preferably there is a washing step or steps prior to curing conditions prevailing for the coating on the surface(s).

5 Preferably said washing step(s) may include exposure to a wetting agent.

Preferably said article is washed prior to treating to a presence of a deactivating agent (eg; of acid(s)). Such preliminary washing may include or may be followed by exposure to a wetting agent prior to the treating of the surface(s) to a presence of (eg) acid(s).

10 In some forms said article also includes a surface or surfaces which is or are other than one of those of the metals or alloys specifically referred to. In some forms the article is an assembly which includes a surface or surfaces (the same or different) having at least in addition, an aluminium or aluminium alloy content.

Preferably said aluminium or aluminium alloy content surface(s) have been
15 anodised prior to the treating of the (anodised or un-anodised) said metal and/or said metal alloy surface(s) to the presence of acid(s).

In still another aspect the invention consists in a method of sealing the or a surface of a material, an article, a component or an assembly (hereafter "article"), being an article having, at least in part, at least one of

20 a magnesium surface,
a magnesium alloy surface,
an anodised magnesium surface. and
an anodised magnesium alloy surface.

which method at least includes the steps of:

25 if the article, at least in part, has an anodised surface, treating the anodised magnesium or magnesium alloy surface to a presence of an acid or acids not substantially destructive of the anodised surface and/or

if the article, at least in part, has a non anodised magnesium or magnesium alloy surface, treating that surface to a presence of an acid or acids not substantially
30 destructive of that surface,

exposing the surface(s) to be sealed to an isocyanate resin suspension whilst a

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cathodic voltage is caused to apply to such surface(s), the surface(s) being substantially free of alkalinity prior to such exposure and the isocyanate resin suspension being such as to be able to provide a coating or coatings on the surface(s) capable of subsequently curing in curing conditions, and

5 subsequently allowing the cure and/or causing the cure of the coating on the surface(s) to provide the seal.

Preferably any of the foregoing methods is performed substantially as herein described with or without reference to any of the examples hereof.

In another aspect the invention consists in an article sealed by a process as
10 previously set forth.

Preferably said article has, in addition to said (anodised and/or un-anodised) metal and/or metal alloy surface(s), anodised and/or un-anodised surfaces of aluminium or of aluminium alloy content.

Preferably said article has a magnesium alloy surface high in aluminium
15 content that has been un-anodised or anodised.

In still another aspect the invention consists in an article having a polymer sealed (anodised and/or un-anodised) surface at least one region of which is of a polymer sealed

metal surface,
20 a metal alloy surface,
an anodised metal surface, and/or
an anodised metal alloy surface,
said metal being an element selected from the group consisting of magnesium, beryllium, titanium, zirconium, hafnium, zinc and aluminium.

25 and wherein said coating has been provided thereto [and, optionally, to other un-anodised and/or anodised surfaces of the article] by means of allowing the cure and/or causing the cure of a coating of the uncured polymer reactants after exposing the surface(s) to be sealed to a curable resin suspension whilst a voltage is caused to apply to said metal, metal alloy, anodised metal or anodised metal alloy surface(s).

30 In even another aspect the invention is a polyurethane (or other polymer) sealed (anodised and/or un-anodised) surface (preferably magnesium and/or

magnesium alloy surfaces). Other surfaces in addition to be sealed may be metallic.

In another aspect the invention consists in, in a process for sealing metal or metal alloy materials (preferably magnesium or magnesium containing) [anodised or unanodised], the use of a dilute HF solution and/or an acid fluoride salt solution (eg
5 $\text{NH}_4\text{F} \cdot \text{HF}$) as a pretreatment of the surface to be sealed by a following electrophoretic process.

Preferably excess HF and/or acid fluoride salt solution is removed and/or dealt with prior to the sealing thereof (eg. by treatment with sufficient CO_3^{2-} or HCO_3^- plus washing).

10 In a yet a further aspect the present invention consists in a method of providing a polyurethane coating to a magnesium containing article comprising the steps of:

- providing an emulsion having the polymerisable requirements of a polyurethane;
- immersing said article in said emulsion;
- 15 - applying a cathodic voltage to the article; and
- once no longer immersed in said emulsion, curing said polyurethane coating on said article.

Preferably said article is pretreated with a mildly acidic rinse followed by either a deionised water rinse or a rinse in dilute glycol ether solution.

20 Preferably said cathodic voltage is in the range of at least 40 volts (eg; 40-70 volts).

Preferably said article is rinsed using a solvent bath and rinse aid prior to curing,

25 Preferably said article is dried and cured at approximately 180°C in preferably a blower oven.

Preferably a dye or opaque pigment is added to the polyurethane emulsion enabling the formation of a coloured polyurethane layer.

The invention also consists in an article thus coated.

All % herein where the context allows are on a w/v basis.

30 BRIEF DESCRIPTION OF DRAWINGS

Preferred forms of the present invention will now be described with reference

to the accompanying drawings in which;

Figure 1 is a flow diagram of a preferred procedure for sealing anodised or unanodised magnesium,

Figure 2 is a flow diagram tying our proprietary magnesium or magnesium alloys (high or low magnesium content) anodising process described hereafter to the sealing process of Figure 1,

Figure 3 is a diagram of the use of a cathodic voltage regime in a process such as that of Figure 1, and

Figure 4 is a cross-section of a sealed anodic surface from a process of Figure 1, showing optional pigment inclusions in the seal.

A seal process that is described herein (using polyurethane as an example) provides a strong, firmly bonded and effective seal, being chemically inert and physically resistant to scratching, abrasion or cracking. This process involves the application of a, as an example, polyurethane polymer by way of electrophoresis followed by a cure cycle. The resulting seal provides a very high specification finish for magnesium articles.

The seal coating is preferably applied to a magnesium anodic film by way of the following steps (see also Figure 1):

- (A) The article, after anodisation, is rinsed thoroughly, preferably in tanks providing a flowing rinse of deionised water.
- (B) Following rinsing, the article is immersed in a deactivating solution preferably containing an acid, such acid being chosen so as not to attack the anodic film unduly while deactivating the surface of the magnesium alloy or anodised magnesium alloy.
- (C) The article is commonly (optionally) prepared for subsequent processing by an immersion in a wetting agent.
- (D) The article is usually conditioned by a rinse in the aqueous phase of the

electrophoretic process, which is sometimes a dilute aqueous solution of a glycol ether such as 1-methoxy propan-2-ol.

- (E) The article is immersed in an emulsion comprising an aqueous phase and oil
5 phase; the latter containing micelles of a blocked oligomer (ie; blocked
polyurethane oligomer if the seal is to be a polyurethane). The oil phase is
preferably present to the extent of from 8 to 15% of the emulsion by weight, and
contains a solvent which is commonly a longer chain glycol ether, such as
hexoxy ethanol.
- 10 (F) A voltage is applied to the anodised article, during which the charged micelles
of resin are drawn towards its surface where they uncurl and deposit, forming a
coating. This coating extends into the pores of any anodic films that might be
present and throws uniformly over the surface of the part. Such voltage may be
either anodic or cathodic depending upon the characteristics of the resin
15 micelles, but as commonly employed, the process is cathodic.
- (G) After a short period, commonly around 70-90 seconds, the article is withdrawn
from the emulsion by means of a rapid action followed by a brief re-immersion
and withdrawal. These cycles wash away polymer that has not properly
20 deposited on the surface of the component which would otherwise cure and form
an uneven coating.
- (H) The article is then preferably spray rinsed with the aqueous phase, removing all
excess polymer.
25
- (I) The article is briefly immersed in a bath containing a wetting agent.
- (J) The article is cured in an oven or by some other method, enabling the oligomer
molecules to cross-link. As this happens, the resin forms a smooth surface of
30 polymer (eg; polyurethane) that is firmly and securely bonded to the anodic film
underneath.

One electrophoretic process for polyurethanes is the TECHNICLAD[®] process, a trademark of Hawking International Ltd, United Kingdom. Other proprietary electrophoretic processes include CLEARLYTE[®]HB a trade mark of Ethone-OMI Inc of USA (an acrylic urethane process) and CLEARLYTE[®] (an acrylic process) a trade mark also of Ethone-OMI Inc.

In our patent specifications PCT/NZ96/00016 (WO 96/28591) and PCT/NZ98/00040 we disclose anodising procedures for a process we refer to herein as our proprietary process and in Table 1 as "Ano". This process has application to at least pure magnesium, magnesium alloys, pure aluminium, aluminium alloys, titanium, beryllium, zirconium and hafnium. Our proprietary anodising process of these patent specifications has application to fabricated structures of different substrates, eg; a fabricated structure of magnesium alloy and of aluminium. Ideally, therefore, so should the sealing procedure. This is in fact the case with the sealing procedure of the present invention.

Description of Electrophoresis

The electrophoretic process may involve (and will now be described by reference to) the application of a polyurethane film to the surface of the magnesium or magnesium alloy anodised part. In a modification of the process it is also possible to coat the surface of a magnesium or magnesium alloy component that has not been anodised. The polyurethane may be deposited alone or together with other substances, whether these substances be dissolved or dispersed in the polymer micelles. Since other substances may be co-deposited, a variety of surface finishes may be obtained, and solvent based dyes or pigments may be added to the resin to yield a wide range of colours to the finished article.

The process is based on emulsion technology in that it comprises a dispersed mixture of two phases, one of which is aqueous while the other is immiscible with water and is based on a solvent, often a glycol ether solution. In effect, the non-aqueous phase consists of tiny droplets which are dispersed throughout the aqueous phase. The size of these droplets is critical to the success of the process and is

controlled in part by regulating the pH of the emulsion.

The aqueous phase of the emulsion also often contains a glycol ether, but one which is miscible in water, such as 1-methoxy propan-2-ol. This aids in the flow of the resin as it deposits on the surface of the substrate and ensures the layer builds up
5 in an even and satisfactory manner.

The resin comprises an oligomer made up of various functional groups including at least one blocked isocyanate. Isocyanate resins polymerise by cross-linking with alcohol groups to form smooth, even polyurethanes which are chemically resistant. These polyurethanes offer a range of favourable surface properties including wear
10 resistance, abrasion resistance, UV absorption and favourable elastic properties. In general, polyurethane coatings are frequently chosen for heavy wear applications as for example on wooden floors where a shiny surface is required over time despite constant wear from use. The blocking of the isocyanate prevents its crosslinking until a raised temperature, such as 137°C, is achieved. This occurs during the curing
15 cycle. Once unblocked, a polyurethane cross-links very quickly.

The resin micelles must also carry an electrical charge as otherwise they would not be attracted to the cathode or anode and therefore not deposit on the surface of the substrate. They are given a charge by ensuring that the resin molecules have a number of ionic sites which in the emulsion form a water soluble negative or
20 positive ion, leaving a nett charge of the opposite polarity within the micelle. In part this is a determinant of micelle size. In a common form of resin, a water soluble organic acid ion is formed. Since this has a negative charge ($R-COO^-$), it leaves behind a positive charge on the oligomer, commonly an amino group ($R-NH_3^+$). As a nett positive charge on the micelle results, it is attracted to a cathode upon the
25 application of a suitable voltage. Another resin ionises yielding a water soluble amine ion ($R-NH_3^+$), leaving a negative charge on the resin. Such a resin is attracted to the anode upon application of a suitable voltage. A disadvantage inherent in using the anodic form as described above is that amine salts tend to encourage the growth of bacteria in the bath leading to contamination and blocked filters. The cathodic
30 version does not have this problem.

Preferred voltage applications include a DC voltage. For example, with

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magnesium in a polyurethane system a voltage range of within 60 to 120 volts would be usual but not mandatory.

The resin molecules are oligomers which feature lengthy, hydrophobic chains of hydrophobic hydrocarbons, to which hydrophilic groups, such as sulphonate or amino are attached. In such molecules, a droplet tends to form in which the hydrophobic parts of the molecule face inwards with the hydrophilic groups projecting outwards into the aqueous solution. In this case, the droplet becomes electrically charged and due to this charge, it repels other droplets of resin. A balance will be maintained where droplet size is dependent upon emulsion pH and the nature of the ionic sites present on the resin micelle. In general, the cathodic versions of this process will operate under acid conditions and the anodic versions under alkaline conditions.

While the foregoing description suggests that this is a relatively simple process in practice it requires very careful attention to pH, emulsion conductivity and the purity of the solvents used in preparing the emulsion. Excessive conductivity would manifest in coating difficulty with a coating either not forming at all or forming unevenly and with no uniformity. In particular, contamination of the system must be avoided and in general, a closed cycle purification loop featuring a filter and an ion exchange resin will help to ensure that conductivity remains low and the emulsion remains free from contaminants that would otherwise cause the precipitation of large clumps of resin. The surface chemistry of the substrate is also of critical importance as the deposition of the resin is a surface reaction and an incompatible surface will prevent the proper deposition of the resin regardless of how well balanced the bulk chemistry of the bath might be.

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Preparation of an emulsion

The active, working emulsion is prepared from the base materials by a careful emulsification process. The addition of water to the resin to prepare a suitable emulsion must be done slowly with adequate blending of the resin and water. That this is so stems from the fact that a fine, even dispersion of resin micelles is required and there is a tendency for insoluble organic materials to form large clumps rather

than even dispersions.

Since it is generally intended to form a dispersion that features a non-volatile concentration of between 8 and 12 percent, a considerable amount of water must be added to reach the desired concentration of resin. This will usually be done progressively. Characteristically, the resin becomes increasingly viscous as water is added and blended with it and at a certain point a maximum is reached. Thereafter, the viscosity decreases. This point is known as an inversion and there is a risk if too much water is added too quickly that clumps of resin at inversion concentration will form with the consequent result that proper dispersion of the resin is not possible.

Since both the aqueous and non-aqueous phase solvents are miscible in each other and the resin is miscible in each, these may be blended with the resin prior to the commencement of the blending process with water. Solvent dyes, or pigments added to produce a coloured film may also be added at this stage and blended with the resin as may other substances as discussed herein. In fact, such materials should be added prior to the addition of any water to ensure even and complete solution or dispersion within the desired phase.

Incorporation of other pigments into the resin

A range of solvent-based dyes is soluble in organic solvents and these may be dissolved in the non-aqueous phase to yield a coloured deposited layer. The layer deposited by means of the electrophoretic process is normally transparent, glossy and clear. By means of dye additions it is possible to create any desired colour. Since the dyes are transparent, however, the lightest shade possible is the base colour of the substrate and in cases where the substrate is itself coloured, either naturally or by means of a treatment carried out prior to sealing, an obvious limit on the range of possible colours results. To obtain a white colour or a very deep black an opaque pigment may be added to the resin and blended with it. In this sense, the resin acts as a carrier for the pigment and deposits an opaque layer on the substrate surface. The desired tone may be obtained by blending pigments. Typically brilliant white shades may be obtained by dispersions of titanium dioxide.

Pigments must be chemically unreactive and neutral in electrical charge. They

may be blended with the resin before the preparation of an emulsion. Dyes must be blended with the resin prior to the addition of any water since these are not soluble in water.

5 Incorporation of matting agents and others species in the resin

The resin provides a smooth, glossy finish. While this satisfactory for many applications, a matt appearance may be desired. It is possible to disperse species such as finely divided silica or mica into the resin to modify the surface appearance of the resin. Such a species must be chemically unreactive and incapable of
10 ionisation as otherwise its presence would affect the delicate balance between the micelle size and the conductivity of the emulsion. Such species must be blended with the resin prior to their addition to the emulsion as otherwise their dispersion within the non-aqueous phase of the emulsion becomes impossible.

Silica may be added to provide a matt finish. As the presence of an inert species
15 such as this reduces the number of surface bonding sites available to the resin its concentration should not be so high that the strength of the bond to the substrate is adversely affected. The gloss levels of the coating gradually decrease as more silica is dispersed into the resin.

Mica may be added to give a metallic appearance similar to that of a metallic
20 paint. This may be used in conjunction with pigments or other colouring agents to yield a variety of metallic paint colours. Again the addition of this species reduces the number of available sites within the resin micelles for surface bonding to the substrate.

In general, a range of materials may be dispersed into the resin in this way, to
25 give altered or enhanced surface properties when the resin is cured. The substances that are infused in this way may include but are not limited to pigments and inert fillers. A requirement of the process is that each candidate for infusion into the resin must be inert and not able to promote the cross-linking of isocyanates. Also, for success, the dispersed species should be relatively close to the density of the resin
30 otherwise there would be a tendency for it to fall out of the emulsion. Metals, which are generally subject to attack over time by bath constituents, particularly the mildly

acidic cathodic resins, are not normally suitable as dispersed fillers.

Sometimes a filler may be chosen to give the sealed film special properties. The polyurethane film resulting from the normal application of the process is highly insulating. Infusion of electrically conductive carbon black may reduce this and even
5 render the film conductive. Care must be taken to avoid an excess of carbon in the dispersion as this disrupts the ionisation and polarisation of the micelles which is so necessary for deposition on the part to be coated.

A problem in infusing such species into the resin micelles is that the stability of the resin is based on a fine balance, both chemically and electrically. Any materials
10 that disrupt this balance may cause micelles to be attracted together, resulting in precipitation of sticky lumps of resin, or alternatively, some agents may even bring about the polymerisation of the resin. In general, the presence of an additional species within the resin micelles requires that continual agitation be employed to ensure the emulsion remains uniform.

15

Curing the resin

As stated, the curing cycle normally involves heating the resin to a sufficiently high temperature so that the isocyanate radicals attached the polymer chains will unblock. These then cross-link, forming a long chain polyurethane polymer.
20 Provided that the isocyanate is unblocked, the process by which the resin is polymerised need not involve the direct application of heat, although in its most common form, it does.

This may be achieved in a conventional oven by heating the parts to be cured to a temperature in excess of 137°C and maintaining this long enough to ensure all
25 resin has unblocked and cross-linked. A common application is to heat the parts to 180°C and maintain the temperature for 30 minutes.

Curing may also be achieved by using infra-red. The curing time required depends upon the infra-red flux, the wavelength of the applied infra-red and the nature of the parts to be cured. In cases where the parts are dark in colour or highly
30 reflective of infrared energy, the curing cycles might be quite short owing to surface heating of the resin. Anodised magnesium articles are generally matt in appearance

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and therefore curing times may be lengthy. A wavelength close to that of visible light is recommended for the most rapid cures, that is, a wavelength from 700 nanometres to 1,200 nanometres.

Ultraviolet light may in some cases also cure the resin, although polyurethane
5 resins absorb ultraviolet light. However, provided the quantum energy of each photon of ultraviolet light exceeds the bond energy of the blocking agent, UV may unblock the resin and promote curing. In its practical application, UV of a wavelength shorter than 220 nanometres cannot be employed since such UV is not transmitted by air. The use of wavelengths corresponding to the ultraviolet-B or C
10 spectrums (UV-B = 285-320 nanometres and UV-C = 220-280 nanometres) is hazardous on account of the propensity of such UV energy to cause melanoma. A suitably enclosed apparatus may be employed for UV exposure within this range. UV exposures within the photo-sensitive range of diazo and photopolymer materials used within the printing and graphic arts trades (360-370 nanometres) may be
15 sufficient to unblock some blocking agents and one modification of the resin is designed to operate as a photoresist material, cured by ultraviolet in precisely this manner.

The photoresist agent may be employed in conjunction with a film positive which is drawn into close contact with the deposited resin. After an ultraviolet light
20 exposure, the film is removed, leaving uncured resin in areas where the film was opaque. A suitable solvent, leaving no polymer in these places may then remove this, while other areas feature a hard, cured surface of polyurethane. Its application to anodised magnesium substrates is as a method of masking, where it is desired to leave certain regions uncoated. Complex shapes may be masked this way where
25 conventional techniques of masking that require the application of a tape or paint, are simply too labour intensive.

Nothing herein stated excludes the use of more than one curing regime, eg; both heating plus UV

30 **Characteristics of magnesium and anodised magnesium surfaces**

Magnesium metal tends to form a surface oxide layer which protects it from

further attack. Though this film is not as well defined as the film that protects aluminium, it prevents the metal from dissolving in water despite the favourable electrochemical potential. In aqueous solution, some dissolution of magnesium oxide occurs resulting in the formation of hydroxide ions. The solubility of magnesium hydroxide in water is about 0.1 milligrams per litre, but this is sufficient for
5 magnesium to exhibit an alkaline reaction with water.

Anodised magnesium components manifest a surface layer which is predominantly magnesium oxide, or which contains a mixture of ingredients such as magnesium aluminate. It is our belief that a basic reaction with water results from
10 hydrolysis therefore, regardless of the chemistry of the anodising process, the surface of the article is essentially alkaline.

Since the electrophoresis resin is extremely dependent upon pH, as this regulates micelle size and ionic charge on the micelle, the surface must normally be made receptive to the resin micelle. Often a deactivation step is required to do this as
15 otherwise the resin will not deposit correctly. A magnesium article, for example, when immersed without deactivation in Techniclad[®] HDXC resin, which is a cathodic electrophoretic resin, will tend to form a thick poorly adherent coating featuring spheres of coagulated resin. This is unusable and represents a failure of the process.

20 If the surface is modified by reaction with a suitable acid, the surface alkalinity no longer exists and the resin deposits normally. To achieve this, the acid must form a sparingly soluble or insoluble magnesium salt as otherwise the magnesium compound formed by reaction with the anodic film will wash off and the surface will still be alkaline by hydrolysis. The acid should not substantially dissolve the anodic
25 film during the films exposure to the acid(s). Lactic acid, for instance, forms magnesium lactate by surface reaction with either magnesium metal or the anodic film and is suitable, although excessive exposure to the acid will result in stripping of the anodic film from the metal substrate.

By contrast, an acid which produces a soluble magnesium salt, for instance,
30 acetic acid, merely dissolves the anodic film without producing a pH neutral film. The use of acetic acid in an attempt to deactivate the surface is generally prone to

failure for this reason. If any magnesium acetate is carried over into the resin bath, it tends to dissolve thereby creating an undesirable increase in the concentration of ions in the bath and as a consequence, the conductivity.

Stearic acid (n-octyldecanoic acid) does not work because, although the
5 magnesium salt is highly insoluble, the acid does not react with either magnesium metal or magnesium oxide and no deactivation results.

Tartaric acid is a good combination of an acid that is sufficiently water soluble to react with the magnesium or magnesium oxide anodic film while providing an almost insoluble magnesium salt that then presents a deactivated surface to the resin
10 micelles.

A problem inherent in deactivating the surface of the magnesium or anodised magnesium article is that the entire surface of the article must be treated. Anodised magnesium features a highly porous structure and it is necessary for the acid to "wet out" the entire surface. Failure to penetrate recesses will result in unacceptable
15 results from resin agglomeration and "cissing".

Another acid that offers a highly insoluble magnesium salt is hydrofluoric acid. Hydrofluoric acid forms magnesium fluoride, MgF_2 , by reaction with either magnesium metal or magnesium oxide. The magnesium fluoride is very insoluble in water and forms a stable, strongly adherent species. ideal for subsequent application
20 of a seal. It may be employed to yield a high quality surface finish on either magnesium metal articles or anodised magnesium articles. As it is important to avoid carry-over of fluoride ions or in fact any extensively ionised species into the resin bath, careful rinsing should be conducted after the immersion in hydrofluoric acid and prior to immersion in the aqueous phase of the electrophoretic process.

25 Judging the end point of a deactivation of the surface is often difficult and for this reason it is advantageous to use an acid that does not yield a significantly water soluble magnesium salt so that the process may be conducted to excess. This way, excess time in contact with the acid solution will not dissolve the anodic film. To some extent, the extent of neutralisation required depends upon the anodisation
30 conditions as the surface structure of the film affects the ability of the acid to wet the surface and react with it to form the resin-receptive structure required for a smooth,

even film to result.

Composite materials

Frequently components comprising two or more different metals are to be coated. These components may feature magnesium or a magnesium alloy connected in some way to an aluminium alloy. Aluminium, while commonly anodised in sulphuric acid solutions, may be anodised in electrolytes used in some magnesium anodisation processes. The film is different in character to that normally obtained from sulphuric acid anodisation.

Aluminium may be sealed using an electrophoretic process as described herein. An anodised aluminium component may also be sealed by such means. An article comprising a magnesium part bonded to an aluminium part may be anodised through the same process then sealed. In such cases, the anodic film covering the aluminium part is different in thickness to that covering the magnesium article.

Beryllium, a metal used largely in military applications, may also be anodised using certain magnesium techniques (eg; our proprietary anodisation process) and then sealed using this technology. Beryllium, though the first member of Group II of the periodic table (in which magnesium also falls), exhibits much behaviour in common with aluminium (which is in Group III). As such, it exhibits amphoteric behaviour and it tends towards considerable covalency in its chemical compounds.

Figure 4 shows a cross-section of a sealed magnesium or magnesium alloy material in accordance with the present invention. The metal or metal alloy substrate 1 is shown having an anodised surface 2 thereof which has been sealed with an appropriate polymer 3 which may optionally include pigment inclusions 4.

Figure 3 shows a preferred apparatus in accordance with the present invention in which

5 is the immersed metal part which acts as the cathode (negative),

6 is the anode (positive),

7 is the emulsion,

8 is the aqueous phase (permeate),

9 is the sparge pipe,

- 20 -

- 10 is the return to the sparge pipe,
11 is the weir (resin overflow),
12 is the ultra-filtration unit,
13 is the permeate return (deionised),
5 14 is the pump,
15 is the feed to the ultra-filtration unit.

The following examples, the data of following Table 1 and the recommendations of following Table 2 further exemplify the procedures of the present invention.

10 **Example 1**

A magnesium alloy plate (AZ91D) was anodised using our proprietary process, creating an anodic film 15µm in thickness. This was deactivated in a solution of lactic acid, comprising 1% lactic acid (2-hydroxypropanoic acid) and 0.01% of a glycol-based wetting agent. The temperature of the deactivating bath was
15 ambient (20°C) and the immersion time in the bath was 2 minutes. Following this, the plate was sealed using a cathodic voltage of 80 volts for 90 seconds, and on inspection it proved to have a uniform film which after curing in an infrared oven for 90 minutes was found to add an additional 15µm to the overall film thickness.

20

Example 2

A magnesium alloy plate (AM50A) was anodised using our proprietary process, creating an anodic film that was found to be 24µm in average thickness using an eddy current meter. This was deactivated in a bath containing 35% hydrofluoric
25 acid for one minute, followed by a brief rinse in a dilute solution of sodium carbonate to neutralise all traces of acid. Another rinse, in deionised water, followed, then the plate was sealed in a cathodic bath using a potential of 110 volts for 90 seconds. The plate was found to exhibit a uniform layer of resin, and on testing following an oven cure at 180°C for 30 minutes, the combined
30 thickness of the anodic film and seal was found to be 29µm.

Example 3

A magnesium alloy plate (AM50A) was partially immersed in 35% hydrofluoric acid for one minute, during which time the surface appearance of the plate darkened slightly as magnesium fluoride formed on the exposed surface. The whole plate was then rinsed in sodium carbonate solution followed by a deionised water rinse. This was sealed using a cathodic process, at a potential of 60 volts for 80 seconds. The plate was found to exhibit a uniform layer of resin where deactivation had been effected by the hydrofluoric acid, with an uneven deposit elsewhere. After curing, the portion of the plate which had been deactivated was found to have a shiny layer of seal of approximately 15µm in thickness.

Example 4

An anodised magnesium alloy plate (AZ91D) possessing a coating thickness of 15µm was deactivated in a benzoic acid solution (0.2%) for twenty minutes. This was then sealed using a cathodic process at a voltage of 80 volts for 90 seconds. The resulting coating manifested some "cissing" comprising small globules of resin, but not to the extent that would have resulted had it not been immersed in the benzoic acid.

Example 5

A titanium clip was anodised, yielding a grey film having a thickness of approximately one micron. Our proprietary anodising process was employed. This was then deactivated in a solution containing approximately 1% w/v lactic acid (2-hydroxy propanoic acid) for around 90 seconds, then sealed in a cathodic process at 60 volts for approximately 90 seconds. A uniform coating of the resin resulted.

Example 6

A sheet of AZ31B alloy magnesium that had been hot rolled and extruded was prepared for anodising in our proprietary process by removal of surface dirt and

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imperfections in an etch bath containing 1.0 molar hydrochloric acid. This resulted in a vigorous effervescence as the etch removed surface metal. The sheet was then treated in the phosphate bath of our proprietary process and anodised to yield a film having a thickness of approximately 25 microns. This
5 was immersed in a 0.5% solution of lactic acid for five minutes, following which it was sealed in a cathodic bath containing a matting agent (a modified silica) together with a mixture of a black and a white pigment. The resin deposit resulting from a cathodic potential of 90 volts and a time of approximately 80 seconds was grey in appearance and cured to yield a matt grey texture in the
10 polyurethane film.

Example 7

A magnesium casting (AZ91D alloy) was anodised to give a coating of around 20 microns using our proprietary process. This was then deactivated in a bath
15 containing 0.5% lactic acid then sealed using a cathodic process to which black pigment had been added, together with a quantity of a blue-black solvent dye. The appearance of the emulsion was deep black in colour, and the resin deposit on the casting was also black in appearance. Upon curing the finished article exhibited a shiny black appearance.

20

Example 8

A magnesium plate, die-cast from AZ91D alloy, was anodised using our proprietary process to a coating thickness of 15µm was deactivated in a lactic acid solution of approximately 0.5% lactic acid, for approximately one minute.
25 The article was then sealed in a cathodic resin bath containing a white pigment dispersed into the resin. The article was sealed using a cathodic voltage of 60 volts and the appearance of the final article was glossy and a brilliant white colour.

30

Example 9

A test plate comprising AZ91D magnesium alloy, was anodised to a thickness of

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25µm using our proprietary process then coloured using our proprietary colouring process described in our PCT/NZ98/00030, specifically a red vinyl sulphone reactive dye. The coloured article was then introduced to a lactic acid solution containing 0.5% lactic acid whereupon there was a pronounced leaching of the colour. The article was still coloured red, and this was sealed using a cathodic clear seal which was applied at a voltage of 60 volts for 80 seconds. The final article had a glossy coat over the red substrate after curing for half an hour in a thermowave oven.

10

Example 10

A magnesium alloy (AM50A) test plate was immersed in 1% hydrofluoric acid for three minutes, during which time visible effervescence ceased. This plate was then rinsed in a dilute solution of sodium carbonate to eliminate any residual hydrofluoric acid carried out of the bath. The plate was rinsed thoroughly in deionised water then sealed using a cathodic process at 70 volts for 90 seconds. The result was a clear, uniform seal after an oven cure of 30 minutes at 180°C. The seal had a thickness of 16µm.

Example 11

A magnesium alloy plate (AM50A) was anodised using our proprietary process, to a surface thickness of 25 microns. This was immersed in 1% hydrofluoric acid for 90 seconds, rinsed in sodium carbonate solution and deionised water, then sealed using a cathodic process at 120 volts for 90 seconds. The result was a uniform clear seal after an oven cure at 180°C for 30 minutes. Following the application of the seal, the combined coating on the magnesium plate had a thickness of 33µm.

Example 12

An anodised magnesium alloy plate (AM50A) was anodised using our proprietary process to a surface thickness of 25µm. This was immersed in a 1% (w/v) solution of tartaric acid (*dl* 2,3-dihydroxy butanedioic acid) for five

minutes during which time there was some visible reaction evident upon the anodised surface. The plate was rinsed and sealed using a cathodic process at 110 volts for 90 seconds. After an oven cure, the surface was found to be clear and uniform. The plate, after sealing, had a surface thickness of 28 μ m.

5

Example 13

A fabricated assembly comprising an extruded section of magnesium alloy AZ31B, a die casting of magnesium alloy AZ91D, aluminium sheet alloy 5005, aluminium extrusion alloy 6063, aluminium alloy 1350 (rod and wire), and
10 aluminium casting alloy LM6 was anodised using our proprietary process. The anodic film thickness was approximately 25 μ m on the magnesium components and about 10 μ m on the aluminium sheet. The resulting anodised assembly was then deactivated using a bath comprising 1% hydrofluoric acid. This was sealed using a cathodic polyurethane resin, operating at 110 V for 90 seconds. The
15 result was a uniform clear, glossy seal having a thickness of approximately 20 μ m.

TABLE 1

Metals, anodising conditions and sealing conditions

	Metal	Alloy	Emulsion Polymer	Anodic or cathodic	Deactivation Process	Anodised?	Comments
5	Magnesium	AZ91D	Polyurethane	Cathodic	1% Lactic acid	15µm Ano	Good quality film
	Magnesium	AM50	Polyurethane	Cathodic	35% HF	24µm Ano	High quality film
10	Magnesium	AM50	Polyurethane	Cathodic	35% HF	None	High quality film
	Magnesium	AZ91D	Polyurethane	Cathodic	0.2% Benzoic acid	15µm Ano	Poor quality film with evident "cissing"
15	Aluminium	6063	Polyurethane	Cathodic	1% HF	4µm Ano	Good quality film
	Titanium		Polyurethane	Cathodic	None	1µm Ano	Failure
	Titanium		Polyurethane	Cathodic	1% Lactic acid	1µm Ano	Good quality film
20	Magnesium	AZ31B	Polyurethane + matt agent	Cathodic	0.5% Lactic acid	25µm Ano	Good quality film
	Magnesium	AZ91D	Polyurethane + pigment	Cathodic	0.5% Lactic acid	20µm Ano	Good quality film
25	Magnesium	AZ91D	Polyurethane + pigment	Cathodic	0.5% Lactic acid	15µm Ano	Good quality film
30	Magnesium	AZ91D	Polyurethane	Cathodic	0.5% Lactic acid	25µm Ano + Colour	Colour fade but good quality seal
	Magnesium	AM50	Polyurethane	Cathodic	1% HF	None	High quality film
35	Magnesium	AM50	Polyurethane	Cathodic	1% HF	25µm Ano	High quality film
	Magnesium	AM50	Polyurethane	Cathodic	1% Tartaric acid	25µm Ano	Good quality film
	Magnesium	AZ91D	Polyurethane	Cathodic	1% HF	25µm Ano + Colour	High quality film and no colour bleed
40	Magnesium	AZ91D	Polyurethane	Anodic	1% HF	None	Good quality film
	Magnesium	AZ91D	Polyurethane	Anodic	1% HF	25µm Ano	High quality film
45	Magnesium	AZ91D	Polyurethane	Anodic	None	25µm Ano	Poor quality with considerable "cissing"
	Magnesium	AZ91D	Polyurethane	Cathodic	1% HF	25µm Tag	High quality film
50	Magnesium	AZ91D	Polyurethane	Cathodic	1% HF	25µm Mag	High quality film
	Magnesium	AZ91D	Polyurethane	Cathodic	1% HF	Dow 17	High quality film
55	Aluminium	6063 extruded	Polyurethane	Cathodic	1% HF	8µm Ano	High quality film
	Aluminium	5005 sheet	Polyurethane	Cathodic	1% Tartaric acid	8µm Ano	Reasonable quality film
60	Aluminium		Polyurethane	Cathodic	None	None	Good quality film
	Magnesium	AM50	Acrylic	Cathodic	None	24µm Ano	Failure
65	Magnesium	AM50	Acrylic	Cathodic	1% HF	24µm Ano	High quality film
	Magnesium	AM50	Acrylic	Cathodic	1% HF	None	Good quality film
	Zinc		Polyurethane	Cathodic	1% HF	None	Good quality film

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	Magnesium	WE43	Polyurethane	Cathodic	1% HF	15µm Ano	High quality film
	Magnesium	MMC ¹⁶	Polyurethane	Cathodic	1% Lactic acid	Ano	Good quality film
5	Zirconium	Std ⁴	Polyurethane	Cathodic	1% HCl	1.8µm Ano	High quality film
	Zirconium	Std	Polyurethane	Cathodic	1% HCl	12µm Ano	High quality film
10	Beryllium	Pure ³	Polyurethane	Cathodic	1% Acetic acid	8µm Ano	Good quality film
	Magnesium	AZ91D	Polyurethane + dye	Cathodic	0.1% Lactic acid	25µm Ano	Good quality coloured film.
15	Magnesium/ Aluminium	AZ31B + AZ91D + (i) 5005 sheet (ii) 6063 extrusion (iii) LM6 die- casting, or (iv) 1350 alloy rod or wire	Polyurethane	Cathodic	1% HF	Mg-25µm, Al-10µm Ano	High quality film on entire component
	Magnesium	AZ91D	Acrylic	Cathodic	1% HF	20µm Ano	High quality film
20	Aluminium	Die- casting alloy LM6	Polyurethane	Cathodic	1% HF	10µm Ano	High quality film

Notes to table:

25 "Ano" indicates the sample was anodised using the Anomag process as discussed herein. The process as applied to metals other than magnesium may involve varied pre-treatments, but the anodising electrolyte is the same for all metals.

"None" in the "Anodised?" column means the metal sample was not anodised prior to sealing.

30 "Colour" in the "Anodised?" column denotes that subsequent to anodising, but prior to sealing, the sample was coloured. This is not the same as colouring using a coloured seal. Where the seal included a colouring agent there is reference in the column headed "Emulsion Polymer" to the inclusion.

35 "Tag" denotes TAGNITE[®], a registered trademark of Technology Applied Group, North Dakota, USA. This is a magnesium anodising process.

"Mag" denotes MAGOXID[®], a registered trademark of AHC Oberflächentechnik, of Germany.

40 "Dow 17" refers to the process, Dow Number 17, as described in a publication of the Dow Chemical Company, USA. No thickness could be given for this anodising, as the coated part did not possess a flat profile so no measurement could be made.

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"Ano" is the coating of our proprietary anodised coating. In some cases the anodic film could not be assessed for thickness as the coated part possessed no flat faces. "MMC" refers to a magnesium MMC (ie; metal matrix composite) which in the specific instance contained 12% silicon carbide.

5

The zirconium alloy used comprised up to 4% hafnium, which is standard in all zirconium ores. The hafnium has identical chemical properties to the zirconium and is not normally removed except for specialist applications such as fuel rod cladding in nuclear power reactors. No other alloying constituents were present.

10

The beryllium sample was pure beryllium metal with no included alloying constituents.

TABLE 2**Recommended agents for different metals**

	Metal	Polymer type	Recommended agents
5	Magnesium alloys anodised or metal (unanodised)	Polyurethane cathodic	Hydrofluoric acid (1%), bifuoride salt, tartaric acid (1%), potassium hydrogen tartrate (60°C, saturated)
	Aluminium alloys anodised or metal (unanodised)	Polyurethane cathodic	Hydrofluoric acid or bifuoride salt (1%)
	Magnesium-aluminium combined	Polyurethane cathodic	Hydrofluoric acid or bifuoride salt (1%)
10	Titanium anodised	Polyurethane cathodic	Lactic acid (1%) or hydrochloric acid (1%)
	Zirconium anodised	Polyurethane cathodic	Hydrochloric acid (1%)
	Beryllium anodised	Polyurethane cathodic	Acetic acid (1%)
15	Zinc metal	Polyurethane cathodic	Hydrofluoric acid or bifuoride salt (1%)

CLAIMS:

1. A method of sealing the or a surface of a material, an article, a component or an assembly (hereafter "article"), being an article having, at least in part, at least one of
- 5 a metal surface,
a metal alloy surface,
an anodised metal surface, and
an anodised metal alloy surface.
- said metal being an element selected from the group consisting of magnesium, beryllium, titanium, zirconium, hafnium, zinc, and aluminium,
- 10 which method at least includes the steps of
- (I) if the article, at least in part, has said anodised surface(s), treating the anodised surface to a presence of a deactivating agent not substantially destructive of the anodised surface and/or
- if the article, at least in part, has said non anodised metal or non anodised metal
- 15 alloy surface(s), treating that surface type to a presence of a deactivating agent not substantially destructive of that surface, such deactivating agent(s) being
- (i) an acid or acids and/or
- (ii) a non-acid agent able to render the surface(s) both incapable of significant ionisation in the suspension and of reaction towards the
- 20 suspension,
- (II) exposing the surface(s) to be sealed to a resin suspension whilst a voltage is caused to apply to such surface(s), the surface(s) being substantially free of surface activity (such as alkalinity or water soluble ions) prior to such exposure and the resin suspension being such as to be able to provide a
- 25 coating on the surface(s) capable of subsequently curing on the surface(s) in curing conditions, and
- (III) subsequently allowing the cure and/or causing the cure of the coating on the surface(s) to provide the seal.
2. A method of claim 1 wherein the deactivated surface(s) of step (I) is substantially
- 30 free of ionisable species.
3. A method of claim 1 or 2 wherein said metal element is selected from the group



- consisting of magnesium, aluminium and alloys of magnesium and/or aluminium.
4. A method of claim 3 wherein the metal element is magnesium.
5. A method as claimed in claim 4 said deactivating agent is an acid or acids selected from those which form a sparingly soluble or insoluble magnesium salt.
- 5 6. A method as claimed in any one of the preceding claims wherein said acid or acids is or are selected from the group consisting of lactic acid, tartaric acid and hydrofluoric acid.
7. A method as claimed in any one of the preceding claims wherein said resin suspension is one which upon curing will provide a polyurethane, acrylic, 10 polyacrylomelamine or epoxy seal.
8. A method of any one of the preceding claims wherein the resin suspension is one which includes water.
9. A method as claimed in any one of the preceding claims wherein said resin suspension includes an polyurethane resin.
- 15 10. A method as claimed in claim 9 wherein said resin suspension includes water, a blocked polyurethane resin and a source of -OH moieties selected from alcohols and glycols.
11. A method as claimed in any one of the preceding claims wherein said subsequent step (III) allowing the cure and/or causing the cure of the coating on the surface(s) to 20 provide the seal results from applying heat or a source of unblocking radiation to the coated surface(s).
12. A method as claimed in claim 11 wherein the heating of step (III) is to above 137°C.
13. A method of any one of the preceding claims wherein the voltage caused to apply 25 to such surface(s) is a cathodic voltage.
14. A method of claim 14 wherein said cathodic voltage is applied in the form of a direct current.
15. A method of any one of claims 1 to 12 wherein said voltage caused to apply to such surface(s) is an anodic voltage.
- 30 16. A method of any one of the preceding claims wherein the surface(s) is or are anodised, prior to such surface(s) being treated to a step (I) presence of acid(s) or other



deactivating agent(s).

17. A method of any one of the preceding claims wherein the step (II) exposing of the surface(s) to the resin suspension is by means of dipping.

18. A method as claimed in any one of the preceding claims wherein there is a
5 washing step or steps prior to curing conditions of step (III) prevailing for the coating on the surface(s).

19. A method as claimed in claim 18 wherein said washing step(s) may include exposure to a wetting agent.

20. A method as claimed in any one of the preceding claims wherein said article is
10 washed prior to a step (I) treating to a presence of acid(s) or other deactivating agent(s).

21. A method of claim 20 wherein such preliminary washing may include or may be followed by exposure to a wetting agent prior to the step (I) treating of the surface(s) to a presence of acid(s) or other deactivating agent(s).

22. A method of any one of the preceding claims wherein said article also includes a
15 surface or surfaces which is or are other than one of those specifically referred to in claim 1.

23. A method of any one of the preceding claims wherein the article is an assembly which includes at least a surface or surfaces having an aluminium or aluminium alloy content.

20 24. A method of claim 23 wherein said aluminium or aluminium alloy content surface(s) have been anodised prior to the step (I) treating of the (anodised or un-anodised) said metal and/or said metal alloy surface(s) to the presence of acid(s) or other deactivating agent(s).

25 25. A method of sealing the or a surface of a material, an article, a component or an assembly (hereafter "article"), being an article having, at least in part, at least one of
a magnesium surface,

a magnesium alloy surface,

an anodised magnesium surface, and

an anodised magnesium alloy surface.



30 which method at least includes the steps of:

if the article, at least in part, has an anodised surface, treating the anodised

magnesium or magnesium alloy surface to a presence of an acid or acids (which may be an acid salt) not substantially destructive of the anodised surface and/or

if the article, at least in part, has a non anodised magnesium or magnesium alloy surface, treating that surface to a presence of an acid or acids (which may be an acid salt) not substantially destructive of that surface,

exposing the surface(s) to be sealed to a resin suspension whilst a cathodic voltage is caused to apply to such surface(s), the surface(s) being substantially free of ionisable species prior to such exposure and the resin suspension being such as to be able to provide a coating or coatings on the surface(s) capable of subsequently curing in curing conditions, and

subsequently allowing the cure and/or causing the cure of the coating on the surface(s) to provide the seal.

26. A method of claim 25 wherein the resin suspension is a water and isocyanate including suspension capable of curing to a polyurethane.

27. A method of any one of the preceding claims wherein the surface(s) are coloured using a dye prior to exposing to the resin suspension and/or the resin suspension includes pigment(s) and/or graphite and/or silica and/or mica.

28. A method of any one of the preceding claims substantially as hereinbefore described with or without reference to any of the examples hereof.

29. An article sealed by a process as claimed in any one of the preceding claims.

30. An article as claimed in claim 29 wherein said article has, in addition to said (anodised and/or un-anodised) metal and/or metal alloy surface(s), anodised and/or un-anodised surfaces of aluminium or of aluminium alloy content.

31. An article of claim 29 wherein said article has a magnesium alloy surface high in aluminium that has been un-anodised or anodised.

32. An article having a polymer sealed (anodised and/or un-anodised) surface at least one region of which is of a polymer sealed

metal surface.

a metal alloy surface,

an anodised metal surface, and/or

an anodised metal alloy surface,



* C L M S *

said metal being an element selected from the group consisting of magnesium, beryllium, titanium, zirconium, hafnium, zinc and aluminium,

and wherein said coating has been provided thereto [and, optionally, to other un-anodised and/or anodised surfaces thereof] by means of allowing the cure and/or
5 causing the cure of coating of the uncured polymer reactants after exposing the surface(s) to be sealed to a curable resin suspension whilst a voltage is caused to apply to said metal, metal alloy, anodised metal or anodised metal alloy surface(s).

33. A polyurethane sealed (anodised and/or un-anodised) magnesium and/or magnesium alloy surface.

10 34. An article of claim 32 or 33 wherein said other surfaces may be metallic.

35. A method of providing a polyurethane coating to a magnesium containing article comprising the steps of:

providing an emulsion having the polymerisable requirements of a polyurethane;
immersing said article in said emulsion;

15 applying a cathodic voltage to the article; and

once no longer immersed in said emulsion, curing said polyurethane coating on said article.

36. A method of claim 35 wherein said article is pretreated with a mildly acidic rinse followed by either a deionised water rinse or a rinse in dilute glycol ether solution.

20 37. A method of claim 35 or 36 wherein said cathodic voltage is in the range of 40-70 volts.

38. A method of any one of claims 35 to 36 wherein said article is rinsed using a solvent bath and rinse aid prior to curing,

25 39. A method of any one of claims 35 to 36 wherein said article is dried and cured at approximately 180°C.

40. A method of any one of claims 35 to 39 wherein a dye or opaque pigment is added to the polyurethane emulsion enabling the formation of a coloured polyurethane layer.

41. A coating formed by a method of any one of claims 35 to 40.

30 42. In a process for sealing metal or metal alloy materials, the use of a dilute HF solution and/or an acid fluoride salt solution as a pretreatment of the surface to be sealed



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by a following electrophoretic process.

43. A process of claim 42 wherein the material surface to be sealed is anodised.
44. A process of claim 42 or 43 wherein the metal is magnesium.
45. A method of any one of claims 42 to 44 wherein HF and/or acid fluoride salt
5 solution is removed and/or dealt with prior to the sealing thereof by treatment with
sufficient CO_3^{2-} or HCO_3^- plus washing.

