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54 Method and composition for surface treatment.

57 A hydrous oxide sol such as a zirconia sol is applied to a solid e.g. metal surface and there cured to form a protective coating. The sol may include an adhesion promoter such as a silane and/or a sub-micron passenger powder. Application to the surface may be in one step, or two steps with the second designed to gel the sol. Depending on the microtexture of the sol and the surface, the treatment can be used to control, by increasing or decreasing, the adhesive properties of the surface to a subsequently applied organic coating, or simply to improve corrosion resistance.

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METHOD AND COMPOSITION FOR SURFACE TREATMENT

This invention relates to methods and aqueous compositions for surface treatment. One purpose of the treatment is to increase the adhesion of subsequently applied coatings, such as paint, lacquer, varnish or adhesive. Another purpose is to decrease adhesion, i.e. to confer non-stick properties on the surface. Yet another purpose is to provide protection for the surface from mechanical and chemical damage. Although the invention is of application to solid surfaces generally, it is of major importance in relation to metals generally, and in particular to aluminium.

Alocrom 100 is the Trade Mark of a commercially available chromium-based pretreatment applied to aluminium before coating with organic finishes such as lacquer on can stock or powder coating on architectural components. Excess chromium solution must be rinsed away before the organic coating is applied. This kind of pretreatment is known as conversion coating. Control of the chromium ions in the rinse water to prevent pollution can be a problem with this formulation.

Accomet C is the Trade Mark of another commercially available chromium-based pretreatment, as described in US Patent 3706603. The composition is applied to a metal workpiece and dried in situ without washing; this is known as a no-rinse pretreatment. Accomet C avoids the chromium pollution problems of Alocrom 100, but is not used on can stock for food or beverages because of the danger of toxic chromates leaching out. It is used as a pretreatment for aluminium components that are to be adhesively bonded together, for example as described in British Patent Specification 2139540.

Alocrom 404 is the Trade Mark of a commercially available pretreatment based on zirconium. This is a conversion coating which requires rinsing, but the absence of chromium reduces pollution problems. The protection is not as good as that provided by Accomet C or by Alocrom 100, but it does find some application in the food industry.

Patent Specifications which describe metal pretreatment systems based on zirconium, often in the form of fluorozirconate, include US 3964936; 4191596; 4273592; 4339310; 4370177; and EPA 61911. (Some of these mention Ti, Si and Hf as alternatives for Zr.) All these are conversion coatings containing dissolved Zr.

US Patent 4623591 describes a method of preparing metal surfaces for adhesive bonding by the application of a metal alkoxide solution, which hydrolyses on the surface to form an amorphous hydrated metal oxide layer. Al alkoxides are preferably used, though Ti, Zr, Fe and Ni alkoxides are mentioned as alternatives. Because these metal alkoxides hydrolyse in the presence of moisture, it is necessary to use them in solution in organic solvents such as toluene, which solutions have short shelf life and major handling, cost and environmental problems.

GB 2107215 and 2134008 describe aqueous compositions based on inorganic sols containing refractory oxides for application to refractory substrates followed by firing to produce coatings for catalytic or electronic applications.

EPA 273698 describes coating compositions to improve adhesion of paints etc, which compositions comprise a silica sol containing a dissolved aluminium or iron salt.

GB 1503934; GB 1411094; US 3248249; EPA 201228; and Chemical Abstract 1987 April 14 106545d: all describe coating compositions based on inorganic sols but which contain hexavalent chromium or molybdenum.

There is a need for a pretreatment system for metal and other surfaces which does not require rinsing and does not contain toxic material such as hexavalent chromium or molybdenum, but which nevertheless improves the adhesion properties of the surface for subsequently applied coatings such as paint, varnish, lacquer or adhesive. It is an object of this invention to fulfil that need.

In one aspect the invention provides a method which comprises applying to a solid surface an aqueous composition comprising an inorganic hydrous oxide sol and curing the composition to form a protective coating on the surface. One way of achieving this is by applying to the surface:

- i) the aqueous composition comprising the inorganic sol to form a layer on the surface,
- ii) a fluid which gels the sol on the surface, the applications being made sequentially in either order, and curing the resulting layer on the surface.

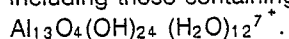
In another aspect the invention provides an aqueous composition for application to solid surfaces, which composition comprises:

- a) an inorganic hydrous oxide sol together with b) and/or c)
- b) an adhesion promotor
- c) from 1 to 300 g/l of a passanger powder having an average primary particle size in the range 3 to 250 nm, provided that the composition does not contain added hexavalent chromium or molybdenum.

The method is suitable for the pretreatment of solid surfaces such as non-metals and metals generally, including steel, titanium, copper, zinc and, particularly aluminium, which term is used herein to include the pure metal and its alloys. The method can be arranged to improve the adhesion properties of the pretreated surface, by improving the adhesion thereto of a subsequently applied coating such as paint, varnish, lacquer or adhesive. The pretreatment may improve either the initial adhesion of the subsequently applied coating to the surface or the maintenance of such adhesive properties in service, or both the initial adhesion and maintenance of adhesives properties. For example, so far as subsequently applied adhesive is concerned, the benefits of the invention may be shown mainly not in the initial adhesive strength obtained, but in the maintenance of adhesive strength in hostile or corrosive environments.

The inorganic sol is a stable, aqueous, colloidal dispersion containing primary particles or aggregates of primary particles, which are smaller than 150 nm. Depending on the nature of the basic colloidal unit, sols can be classified into three types; type A, B and C.

Type A sols consist of basic units which are polynuclear ions which form an 'inorganic polymer' and are formed by hydrolysis and polymerisation of monomeric cations. The molecular weight of the polynuclear cations will depend on the degree of hydrolysis but these sols normally have an anion to metal ratio of approximately 1:1. The polymeric species are not large enough to scatter light efficiently, so the sol and the resultant gel are optically clear. The gel has a high density, low porosity and the x-ray diffraction pattern consists of very broad bands. J. D. F. Ramsay "Neutron and Light Scattering Studies of Aqueous Solutions of Polynuclear Ions. Water and Aqueous Solutions", 207-218 1986 (ed G. W. Neilson and J. E. Enderby: Bristol. Adam Hilger). Type A sols may be formed from the polynuclear ions listed in this paper by including those containing Al(III) Fe(III) Zr(IV) Th(IV) : for example:



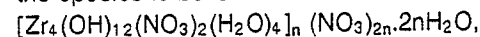
Type B sols consist of basic units with a definite shape, e.g. spherical, rod or plate-like, and are amorphous or microcrystalline. The sol is formed by extensive hydrolysis of a salt and has a low anion to metal atom ratio of approximately 0.3:1. The sols can also be prepared by peptization of fresh precipitates. The colloidal units are not aggregated and the sol and the resultant gel are both clear. Type B sols include (Al(III) Zr(IV) Ce(IV) Ti(IV) Fe(III)). Preparation of Type B Al(III) sols is described in GB 1,174,648. Preparation of Ce Type B sol is described in GB 1,342,893. Type B Alumina Sols are available commercially.

In the type C sol the basic colloidal units are aggregated. They are crystalline and the gels formed by removal of water have a low density. These sols scatter light and are therefore opaque. The sols formed from ultrafine powders prepared by vapour phase techniques, i.e. flame hydrolysed powders, belong to this category.

Type A and B sols when dehydrated yield gels which are >45% of the theoretical density of the oxide. The gels derived from a type C sol are porous and have a density <45% of the theoretical density of the oxide.

The inorganic sol for use in this invention is a hydrous oxide sol, preferably to hydrous metal oxide sol, that is to say a Type A or Type B (but not Type C) sol. Examples are zirconia sols, ceria sols, titania sols, hafnia sols, alumina sols, and iron oxyhydroxide sols. Silica sols exemplify non-metal oxide sols.

Zirconia sols are readily formed by peptising basic zirconium carbonate in mineral acid. The constitution of zirconia sols when the associated anion is nitrate or bromide or chloride is discussed in a UKAEA Research Group Report, reference AERE - R5257 (1966) by J.L. Woodhead and J.M. Fletcher. Zirconia sols contain extensively hydrolysed inorganic polymers with a primary particle size of less than 10 nm. The polymer is thought to be built up of hydrated oxy-hydroxide species of zirconium. When nitric acid is used, the species is believed to have the formula:



where n is thought to be approximately one in dilute sols and greater than one at higher concentrations. Ceria and titania and other hydrous metal oxide sols may be formed by peptising the corresponding hydrated metal oxide with a mineral acid.

Also applied to the surface, according to one aspect of the invention, is a fluid which gels the sol and/or a powder passenger on the surface. For example, Al_2O_3 powder passenger may be gelled on the surface by phosphoric acid. This fluid may be in vapour phase, for example a low molecular weight amine such as ethylamine or preferably ammonia, which is applied after the aqueous composition and simply serves to gel and thereby fix the layer on the surface. More preferably, the fluid is a liquid, particularly an aqueous liquid containing a gelling agent for the sol. This liquid may be applied to the surface to deposit the gelling agent thereon, prior to application of the inorganic sol. Alternatively, the liquid can be applied to the surface already carrying a layer of the inorganic sol. It is preferred, though not essential, that the layer of inorganic sol be dried prior to application of the gelling fluid. Gelling of the layer causes or may cause shrinkage, and care may need to be taken to prevent cracking of the layer at this stage. Drying may be effected at

temperatures below 100°C, conveniently at ambient temperature.

Either the aqueous composition i) or the fluid ii) may contain an adhesion promoter. These materials may also act as gelling agents for the sol. The two step method of this invention allows the incorporation of high concentrations of these reagents into the fluid ii).

Because the composition is intended for a no-rinse treatment, the dissolved adhesion promoting constituent should preferably be substantially non-toxic. The constituent promotes adhesion, for example by providing suitable links to the underlying substrate and to the overlying organic layer, or by inhibiting corrosion at the organic coating/substrate interface. It is believed that adhesive bond strength falls on exposure to water or more aggressive agents because of corrosion or hydration at this interface. Inhibition of this corrosion helps to retain adhesive bond strength.

Adhesion promoters are known and employed to enhance the joint strength, or more commonly to enhance the environmental resistance of the substrate surface/adhesive interface to attack by moisture. Adhesion promoters were described by P.E.Cassidy et al in Ind. Eng. Chem. Prod. Res. Development, Vol 11, No.2 (1972) pages 170-7; and by A.J.Kinlock in J. Mat. Sci., 15 (1980) pages 2141-66 at page 2159. But these articles do not discuss coating compositions.

The adhesion promoter may comprise fluoride values and one or more of Ti, Si, Hf and Zr values. These can be provided separately. They may conveniently be provided by dissolving fluorozirconic acid H_2ZrF_6 , or a soluble fluorozirconate salt, in water; alternatively, a corresponding acid or salt of Ti, Si or Hf, e.g. H_2TiF_6 , H_2SiF_6 or H_2HfF_6 , may be used. Fluorozirconate (or other fluoro complex) is preferably present at a concentration of 0.1 to 200 gl^{-1} , particularly from 10 to 100 gl^{-1} , of the fluid ii). When provided separately, the fluoride and zirconium (or other) values are preferably sufficient to give a fluorozirconate (or other fluoro complex) concentration in this range.

The adhesion promoter may comprise phosphate or phosphonate, preferably in a concentration of 0.05 to 200 gl^{-1} , particularly 10 to 100 gl^{-1} , of the fluid. Phosphate esters are known to bond well onto aluminium surfaces and to be able to inhibit corrosion. In addition to the phosphoric acids and inorganic phosphates, there are a number of organic phosphorus-containing compounds which may be used, examples being amino-phosphates for example nitrilotris (methylene) phosphonic acid (NTMP) or other nitrilo-substituted phosphonic acids or phosphate esters such as bis-(nonyl phenyl ethylene oxide) phosphate.

The adhesion promoter may comprise one or more silane coupling agents which are organosilanes, for example glycidoxypropyltrimethoxy silane or aminopropyltriethoxy silane, which may act to promote adhesion, preferably in a concentration of 0.05% to 10% by volume on the volume of the fluid. One or more of these or other classes of substantially non-toxic dissolved adhesion-promoting and/or corrosion-inhibiting constituents, including zirco-aluminates, and organo-metallic trivalent chromium compounds, may be used.

The terms fluorozirconate, phosphate etc. are used herein to include the free acid as well as salts and esters thereof.

The adhesion promoter may be an oxidizing agent for the surface. Examples are the Ce^{4+} species, which may be provided in the form of a hydrated ceria sol or as a dissolved ceric salt, and permanganate. The oxidizing agent acts on the aluminium or other metal (e.g. iron or steel) or non-metal surface, improves adhesion of the surface to the protective coating formed by drying the composition, and should be used at a concentration designed to achieve these ends.

The aqueous composition or the fluid may also contain a powder passenger, which can be used to give the protective coating a desired surface topography. The powder is preferably an inert metal oxide such as silica, zirconia, titania or alumina. This may be a type C sol, or a powder produced by comminution, for example. Powder loadings of 1 to 300 gl^{-1} , preferably 5 - 150 gl^{-1} , more particularly 10 - 75 gl^{-1} are appropriate. The powder may have an average particle size below 250 nm, e.g. in the range 3-150 nm, particularly 4 - 100 nm, and is preferably of substantially uniform particle size.

Preferably the powder passenger is present in the aqueous composition containing the inorganic sol. It is possible to incorporate the powder passenger in the fluid ii), provided that the fluid does not react and/or destabilise the powder passenger, as for example when phosphoric acid is added to an Al_2O_3 powder. When this fluid brings about gelation of the sol, the powder becomes incorporated in the layer on the metal surface.

The aqueous composition generally has an acid pH, typically in the range 1.5 to 7. Sol concentration is chosen to achieve a convenient application viscosity. The sol may typically contain from 1 to 200 gl^{-1} metal oxide equivalent. The adhesion promoting constituent when used in the aqueous composition may be present in conventional concentrations, for example from 0.001% to 10% by volume.

A particularly preferred aqueous composition comprises:

a) a zirconia sol of concentration 1 - 200 gl^{-1} metal oxide equivalent,

b) a silane coupling agent present at a concentration of 0.05% to 10% by volume on the volume of the sol, and

c) a passenger powder selected from silica, alumina, zirconia and titania, having an average particle size in the range 3 - 150 nm, and present at a concentration of 5 - 150 g/l⁻¹.

5 The surface to which the aqueous composition is to be applied may be cleaned by conventional means appropriate to the substrate concerned. For aluminium this may be an acid or alkaline cleaning treatment, using commercially available chemicals such as those sold by ICI under the trade marks Ridolene 124 and 124E. Alternatively, the (aluminium or titanium) metal surface may be pre-treated to form thereon an artificially applied oxide layer. Such treatments include acid etching (Forest Products Laboratories), and
10 anodizing treatments with sulphuric, chromic or phosphoric acid, the latter being particularly effective in terms of bond strength and durability. It has been shown by means of transmission electron microscopy that phosphoric acid anodizing treatment produces fine oxide protrusions of greater length and magnitude than other surface treatments. These whiskers are believed to account for the strength enhancement achieved with joints made using phosphoric acid anodized adherends. Thus, mechanical interlocking by
15 whisker reinforcement of an adhesive appears to play a role in enhancing adhesive bonding.

By virtue of their small sol particle size, less than about 0.2 microns and typically less than 10 nm, the aqueous compositions of this invention can be applied to such profiled surfaces in layers so thin and uniform that the profiled surface topography is substantially maintained. It is believed that the artificially applied oxide layer provides improved initial adhesion for subsequently applied artificial coatings by
20 mechanical interlocking; and that the protective coatings applied according to this invention ensure that the initial excellent adhesion properties are not reduced on prolonged exposure to humid or corrosive environments.

Addition of an adhesion promoter to the sol in a controlled manner, i.e. slowly with stirring, results in a clear, homogenous sol with no apparent flocculation. The coating produced by such a pretreatment is
25 therefore smooth and featureless. Or the adhesion promoter can be included in the gelling fluid ii).

If the adhesion promoter is added in a less controlled manner, irreversible flocculation occurs and a turbid pretreatment sol is obtained. Consequently, the coating deposited on the surface is more textured. With silane coupling agents, addition of water to the silane (rather than the recommended procedure of adding the silane reagent to water) results in the formation of condensed polysiloxanes which also
30 contribute to surface microtexturing.

The adhesion to non-metal or metal substrate of subsequently applied organic coatings such as paint, lacquer, varnish or adhesive, depends substantially upon the properties of two interfaces:

i) the interface between the substrate surface and the protective coating with which this invention is concerned;

35 ii) the interface between this protective coating and the subsequently applied organic coating

By control over the microtexture of the protective coating, a number of options are possible:

a) The substrate surface, to which the aqueous composition containing the sol is applied, is clean and flat (or at least not deliberately profiled on a microscopic scale). Although a sound interface i) can perfectly well be formed using the sol alone, it may be advantageous to include an oxidizing agent or adhesion
40 promoter in the aqueous composition or in the gelling fluid ii). So far as interface ii) is concerned, it is possible to give the protective coating some microtexture, by effecting controlled flocculation of the sol and/or by incorporating a passenger powder in the aqueous composition or the gelling fluid. This has the effect of increasing adhesive bond strength, particularly peel strength. Or the protective coating may be made smooth and featureless. This has the effect of reducing adhesive bond strength, particularly peel
45 strength. The coated surface may indeed have non-stick characteristics. Particularly by control over the concentration and size of the passenger powder particles, the adhesion properties of the coated surface can be optimised for its intended purpose.

b) The metal surface has been provided with a textured oxide film (or has itself been profiled on a microscopic scale). So far as interface ii) is concerned, the use of an oxidizing agent is possible but
50 probably not advantageous. As noted above, the protective coating formed is preferably so thin and uniform that the profiled surface topography is maintained at interface ii). For this purpose it is generally preferred that the sol be not flocculated and that a passenger powder be not present although a dissolved adhesion promoter may be advantageous.

The composition may be applied to the substrate surface (optionally carrying an artificially applied
55 oxide layer with a profiled surface) by any convenient technique, such as spin coating, immersion, flow or roller coating, brushing, or by spraying. For aluminium strip, roller coating is likely to be an attractive option. The formulation may need to be adjusted to provide a convenient viscosity for application by the desired method. After application and drying, the coating on the surface is cured. Curing temperatures are from

ambient up to 700°C, usually (though not always) below those required to fully sinter the particles, and may typically be in the range 50 to 400°C. Calcination of the coating at temperatures above 400°C is possible but not usually necessary. For optimum adhesive bond strength, curing temperatures in the range 50 - 100°C are preferred. For good adhesion combined with good protection from corrosion, curing temperatures in the range 100°C to 400°C are preferred. Removal of water takes place progressively and is still not complete at 400°C.

The surface preferably carries the coating at a rate of from 0.01 to 5 gm⁻², preferably between 0.02 and 0.7 gm⁻², and most preferably from 0.05 to 0.3 gm⁻². Thinner coatings up to 1.5 gm⁻² will normally be preferred when the metal surface has been provided with an underlying artificially applied oxide layer. The invention envisages as an additional method step the application to the protective coating of an organic coating such as paint, lacquer, varnish or adhesive. There is increasing interest in the use of adhesively bonded aluminium components as structures for motor vehicles. An example of a commercially available epoxy adhesive suitable for this application is Permabond ESP105.

When the coating is intended for use as a protective coating in its own right, thicker coatings e.g. of up to 5 gm⁻² may be preferred and passenger powders with average particle sizes up to 1 micron or even up to 5 microns may be used.

The following examples illustrate the invention.

Examples 1 to 10

Zirconia sol preparation

In a typical preparation 2 kg of zirconium carbonate (44.8 w/v ZrO₂, 7.2 moles) was added with stirring to 0.9l of 8M HNO₃ (7.2 moles), the paste rapidly dissolved (exothermic 43°C) to give a sol containing 444 gl⁻¹ ZrO₂ equivalent. When cooled to 20°C the dispersion (NO₃/ZrO₂ mole ratio = 1.0) has a viscosity of 16 cp and a density of 1.55 g/cm³.

For pretreatment, the sol was diluted to 10% or 2% of the original concentration. Further dilution also occurred as a result of mixing the sols with equal volumes of solutions of the adhesion promoters. This mixing was effected by dropwise addition with stirring, thus without significant sol flocculation, and as a result the protective coating had a smooth, glassy appearance under the microscope. Volumes used are summarised in Table 1.

TABLE 1

Pretreatment Solutions Prepared for Adhesive Bonding

EXAMPLE

- 1) 2% Zirconia Sol
- 2) 10% Zirconia Sol
- 3) 10% Zirconia Sol and 1% (v/v) Silane coupling agent A1100 (3-aminopropyltriethoxysilane)
- 4) 2% Zirconia Sol and 0.5% (v/v) Silane coupling agent A1100.
- 5) 10% Zirconia Sol and 10% (v/v) Fluorozirconic Acid
- 6) 10% Zirconia Sol and 4% (v/v) Fluorozirconic Acid
- 7) 10% Zirconia Sol and 0.1% (v/v) Phosphoric Acid
- 8) 2% Zirconia Sol and 0.1% (v/v) Phosphoric Acid
- 9) 2% Zirconia Sol and 0.01% (v/v) Phosphoric Acid
- 10) 10% Zirconia Sol and 0.1% (v/v) NTMP (nitrilotrismethylene phosphonic acid)

Sample Pretreatment

300 x 100 panel of 5251 alloy were vapour degreased and then acid cleaned by a 1 minute immersion in Ridolene 124 acid cleaner at a temperature of between 55 and 60°C. Following cleaning, the samples were thoroughly rinsed in deionised water and pretreated by spin coating. Surfaces were thoroughly wetted with the pretreatment solution prior to spin coating. All pretreatments were dried in an oven at 200°C for 1 minute. Additional samples of metal pretreated with the additive-free formulations were dried at 100°C.

Preparation and Tensile Testing of Adhesive Joints

Samples were cut to a width of 20 mm, stacked (ca 12 samples) and cut to a length of 90 mm. A single part epoxy adhesive containing 1% ballotini was applied to one end of two specimens. Specimens were mounted in a jig giving 10 mm overlap, clipped together, and subsequently removed from the jig and cured at 180°C for a time of 30 minutes, commencing from the time the sample temperature reached 175°C. Following curing, excess adhesive was filed off the edges of the sample and, finally the same edges were smoothed with emery cloth.

Samples for accelerated testing were immersed in deionised water at 60°C for 200 hours. All samples were tested on a Zwick tensile tester using a crosshead speed of 2 mm min⁻¹.

Preparation and Peel Testing of Adhesive Joints

Pretreated sheets were then cut to form 20mm x 100mm coupons, bent to form L-shaped adherends and bonded, with a standard heat-cure single-part structural epoxy adhesive, to give T-shaped joints with a 60mm long bondline. These were peeled at 5mm/min on an Instron 1115 tensile tester and the steady-state peel load was recorded during the peel event.

TABLE 2

Effect of Storage at 60°C in water for 200 hours				
Tensile Adhesive Bond Strength kN				
Example	Stored in Dry Environment	Stored in Wet Environment	% Retention of Adhesion	Dry Peel Strength (N)
1) Dried 200°C	4.80 ± 0.29	3.63 ± 0.15	75.6	23 ± 1.5
2) Dried 200°C	4.63 ± 0.16	3.45 ± 0.20	74.5	20 ± 0.6
1) Dried 100°C	5.58 ± 0.78	3.73 ± 0.27	66.7	21 ± 1.0
2) Dried 100°C	4.31 ± 0.10	3.41 ± 0.35	79.1	19 ± 0.6
3)	4.72 ± 0.21	4.22 ± 0.25	89.4	22 ± 1.0
4)	5.38 ± 0.07	5.00 ± 0.19	92.9	30 ± 1.1
5)	3.64 ± 0.03	1.65 ± 0.18	45.3	
6)	3.44 ± 0.26	2.37 ± 0.15	68.9	24 ± 1.1
7)	4.41 ± 0.04	3.73 ± 0.12	84.5	21 ± 1
8)	4.81 ± 0.17	3.85 ± 0.24	80.0	28 ± 7.2
9)	4.70 ± 0.09	3.55 ± 0.04	75.5	27 ± 6.9
10)	4.79 ± 0.10	3.27 ± 0.11	68.3	20 ± 0.6
Etched* (comparative)	5.44 ± 0.02	3.34 ± 0.08	61.4	34.26

*Vapour degreased and acid cleaned as above.

Results

The results of the tests are set out in Table 2. These show that high initial tensile bond-strengths and good bond-strength retentions were obtained both with and without an adhesion promoter. Particularly with fluorozirconate as the adhesion promoter, the compositions led to protective coatings of exceptionally

uniform thickness containing uniformly sized particles, well adapted to allow underlying profiled surfaces to show through. Use of a silane coupling agent as adhesion promoter resulted in exceptionally high initial tensile bond strengths and bond strength retention. The peel strengths reflect the fact that the protective coatings had a smooth finish without microtexture.

5

Example 11

Treatment solutions were prepared and coated as described in Examples 1 to 10 except that dilution with the adhesion promoter was done quickly causing some flocculation of the sol. Coatings produced from the treatments were microtextured.

Example 12

15

Treatment solutions containing silane adhesion promoters were prepared and applied as described in Example 11 except that the silane was diluted to 0.5 volume percentage by adding water to the silane A1110. (The recommended procedure is to add the silane to water.)

The coatings were microtextured.

20

Examples 13 to 19

Various aqueous compositions according to the invention were made up by the general procedure given in Examples 1 to 10. Sample pretreatment and preparation and testing of adhesive joints were also as described in Examples 1 to 10. Details of formulations and peel strengths are set out in Table 3 below.

Silica - Aerosil 380, crystallite size 7 nm

Aerosil 200, crystallite size 12 nm

Alumina - Degussa, flame hydrolysed powder, crystallite size 20nm (Alumina C).

30 Zirconia - Tosoh TZO powder, crystallite size 27 nm, aggregate particle size 400 nm.

The powder was always the last constituent to be added, i.e. it was added to the final sol/adhesion promoter or sol/oxidising agent mixture, with mixing for 1 hour in a Silverson high shear blender to ensure good dispersion.

Ceria sol - Oxidising sol

35 $\text{Ce}(\text{SO}_4)_2$, KMnO_4 - Oxidising agents (salts).

Preparation of a Ceria Sol

40 250g of 99-grade, Rhone-Poulenc Ceria hydrate (typically 70.9 wt% oxide) was slurried in distilled water. 16ml of conc. HNO_3 in 34ml of water was added to the slurry and stirred thoroughly. The mixture was heated to 70°C for 30 minutes allowed to cool and then to settle. The supernate was decanted and water added to the residue to give a final volume of 417ml. The residue immediately disperses to give a stable sol of 425 g l^{-1} concentration.

45 For pretreatment the sol was diluted to 10% or 2% of the original concentration. 0.1M ceric salt, $\text{Ce}(\text{SO}_4)_2$, was added dropwise to the ceria sol, while stirring rapidly, such that minimal flocculation occurred. The 1.5% silica was added finally.

Preparation of a Titania Sol

50 20l of dilute (0.3M Ti) titanium IV chloride solution was added with stirring to 200l of 0.175M NH_4OH (22°C). The gelatinous precipitate was allowed to settle (2hr), the supernatant decanted off, and the precipitate washed with 220l of demineralized water. To remove adsorbed ammonium ions the pH of the washed slurry was adjusted to 3.3 with 1M HNO_3 (approx. 40l) with a pH of 3.8 and a conductivity of 1.3×10^2 umhos. This slurry was then deaggregated by adding 0.75l HNO_3 (pH of slurry 2.3) and allowing to age for 14 days at 23°C. The dilute sol was then evaporated at 20°C to yield a redispersible gel with a characteristic 'glitter'. The gel contains 80.8% TiO_2 .

For pretreatment a 5wt% titania sol was prepared by dispersing the gel in deionised water. The stock sol was dilute further for use in formulation 5.

5 Zirconia Sol and Oxidising Agent

The zirconia sol was diluted to 10% of the original conc. 0.1M KMnO_4 solution was added dropwise to the sol while stirring rapidly such that minimal flocculation occurred. The 1.5% silica powder was added finally.

TABLE 3

Example	Pretreatment	Dry Peel Strength (N)
13	2% Zirconia Sol 2.5% (w/v) Silica	51.6 ± 2.7
14	2% Zirconia Sol 0.5% (v/v) Silane 2.5% (w/v) Silica	58.3 ± 13.9
15	10% Zirconia Sol 0.1% (v/v) Phosphoric Acid 2.5% (w/v) Silica	62.9 ± 3.9
16	2% Zirconia Sol 0.5% (v/v) Silane 1.5% (w/v) Alumina	62.6 ± 1.2
17	10% Ceria Sol 1.5% (w/v) Silica	58.7 ± 1.8
18	2% Ceria Sol 0.2% (v/v) 0.1M $\text{Ce}(\text{SO}_4)_2$ 1.5% (w/v) Silica	60.4 ± 4.4
19	10% Zirconia Sol 1% (v/v) 0.1M KMnO_4 1.5% (w/v) Silica 2% Alocrom 404 (Commercial pretreatment)	54.8 ± 6.8 32 ± 0

EXAMPLE 20

(a) (Prior method). A 1.5% zirconia sol was prepared by methods described in Examples 1 to 10. 10% by weight on the weight of the diluted sol of silica powder (aerosil 380, particle size 7 nm) was mixed in to the sol. The resulting mixture was roll coated onto a clean aluminium surface and dried at 200°C. The value of the coating as a base for adhesive was determined as described above, using a single part epoxy adhesive. The peel strength was measured at 33N.

(b) (This invention). The zirconia sol/silica powder mixture of (a) was roll coated onto cleaned aluminium metal and dried at room temperature to form a layer on the surface. A 7.5% aqueous solution of aluminium dihydrogen phosphate was roll coated onto that layer. The resulting layer was cured at 200°C to form a protective coating on the metal surface. The adhesive peel strength obtained using this protective surface was measured at 65N.

Application of the 7.5% aluminium dihydrogen phosphate solution gelled the zirconia sol in the layer on the metal surface. If that solution had been added to the sol in bulk, uncontrolled flocculation would have taken place and the resulting composition would not have been useful for metal treatment.

EXAMPLE 21

A 2.25% aqueous solution of aluminium dihydrogen phosphate, $\text{Al}(\text{H}_2\text{PO}_4)_3$, was roll coated onto cleaned aluminium metal (AA5251 canning alloy) and dried at room temperature. An aqueous dispersion consisting of 1 volume % zirconia sol and 7 weight % silica powder (Aerosil 200 (supplied by Degussa), particle size 12 nm) was then applied by roller coating on the phosphate coated metal. The resulting coating was cured at 80°C for 3 minutes.

Lacquers were applied to the treated panels and then drawn into standard shaped cans. The four lacquer systems applied and the adhesion test conditions used are standard in the field.

After tests, each sample was assessed for performance and marked semi-quantitatively. An overall impression of performance was obtained from the total marks. For any test, if there were no defects a score of 0 was given and for the word performance a score of 4 was given. Each testing system generates a score from 0 to 16 and the four together generates a score from 0 (best) to 64 (worst). Results are set out in Table 4. A low score is a good result in these tests.

The pretreatment applied on a lacquered surface prevents 'feathering'. Feathering refers to the degree of detachment of a lacquer film from a surface in a ring-pull-tab configuration.

The feathering test was carried out by applying an organosol lacquer on the pretreated surface of an aluminium coupon. The lacquered coupon was sterilised in water at 130°C for 1 hour. Parallel lines were scribed on the reverse side of the metal and the metal was then scrolled back along the scribes. Feathering was assessed by noting the extent of detachment of lacquer along the metal edge. A score of 0 indicates best performance (i.e. no feathering) and a score of 4 indicates poor performance. Results are set out in Table 4.

TABLE 4

LACQUER TESTS		
PRETREATMENT	SCORE	
	LACQUER	FEATHERING
1) Degreased and acid cleaned	40 $\frac{1}{2}$	4
2) ALOCROM 4040 (a commercial nonchromate pretreatment manufactured by AMCHEM supplied by ICI)	34	4
3) 1st coat : 2.25% $\text{Al}(\text{H}_2\text{PO}_4)_3$ 2nd coat : 1% ZrO_2 sol + 7% silica powder	18 $\frac{1}{2}$	2
4) 0.5% ZrO_2 sol 1% Glycidoxy silane 7% Zirconia powder	30	2

EXAMPLE 22

A pretreatment formulation containing 3 components (i.e. the sol, the adhesion promoter and the passenger powder) was prepared as follows:

8 ml of silane (3-aminopropyltriethoxysilane) was added with stirring to 1l of deionised water. 10 ml of conc. zirconia sol (containing 444g/l ZR_2 equivalent) was then added dropwise with stirring in the silane solution. 40g of silica powder (Aerosil 380) was finally blended in and the mixture was homogenised for 1 hour in a Silverson high shear blender to ensure good dispersion.

A second formulation containing a higher sol concentration and a lower silane concentration and a series of other formulations containing a range of chemistries were prepared in a similar manner.

The pretreatment formulations were applied on precleaned aluminium by roller coating and dried at 80°C for 3 mins. The concentration of constituents in the respective formulations, the peel strength of resultant adhesive joints (using a modified epoxy adhesive), the tensile adhesive bond strength and bond strength after 200 hours and 1000 hours of immersion in water maintained at 60°C, are given in Table 5. The results are compared with Alocrom 4040, a commercial pretreatment based on fluorozirconic acid and applied by

dip coating at 30° for 10 mins. and dried at 120°C for 3 mins., as recommended by the supplier (ICI).

TABLE 5

FORMULATION	CONC. OF CONSTITUENTS	TENSILE ADHESIVE BOND STRENGTH (KN)			DRY PEEL STRENGTH
		DRY	200h	1000h	
1	1% ZrO ₂ sol 0.8% Amino silane 4% Silica A380	4.5	4.1	4.1	73
2	5% ZrO ₂ sol 0.5% Amino silane 4% Silica A380	4.0	3.9	3.9	78
3	1% ZrO ₂ sol 0.5% Amino silane 6% Alumina 'C'	4.3	4.2	4.2	74
4	0.5% ZrO ₂ sol 1% Glycidoxysilane 10% Silica A200	4.9	4.4	-	55
5	1.3% TiO ₂ sol 1% Glycidoxysilane 7% Alumina 'C'	4.8	4.4	-	42
6	1.4% CeO ₂ sol 4% Alumina 'C'	4.4	3.9	-	-
7	1% ZrO ₂ sol 0.25% Ce(SO ₄) ₂ 6% Silica A380	4.4	3.9	3.6	39
8	Alocrom 4040	3.7	1.9	1.4	56
(- No data available)					

EXAMPLE 23

Formulation 3 described in Table 5 was used to prepare single lap adhesive joints which were stressed to 8MPa by means of a calibrated spring arrangement and exposed to condensing humidity of 98-100%, in a test cabinet. The joints remained intact after 100 days of testing. Comparison joints made using Accomet C failed after 87 days.

EXAMPLE 24

5% zirconia sol was roller coated on aluminium foil which had been precleaned by vapour degreasing and acid etching. The coating was cured at 450°C for 3 mins.

The coated foil was then used to line a petri dish and 20g of 1% Oxalic acid was heated in the lined container at 50°C for 1 hour. A control experiment with uncoated aluminium foil was also carried out. The Al content in the processed oxalic acid is shown in the following table. (Table 6).

TABLE 6

ALUMINIUM FOIL	CONC. OF Al (ppm)	CONC. OF Zr (ppm)
Uncoated	24	1.8
Zirconia coated	7	1.7

EXAMPLE 25

CR2 steel was precleaned by degreasing, abrading and degreasing again. A pretreatment formulation containing 4% ZrO₂ sol, 2% Amino silane and 7% A200 silica and prepared according to the procedure described in Example 22 (formulation 1), was roller coated on the steel surface. The coating was dehydrated at 180°C for 3 mins. Single lap adhesive joints were prepared with the pretreated metal and the joints exposed to neutral salt spray (5% NaCl) maintained at 43°C. The lap shear strength of the joints were measured at various intervals and compared with lap shear strengths of adhesive joints prepared with electrogalvanised steel. The sol pretreatment resulted in superior performance. The results are given in Table 7.

PRETREATMENT	LAP SHEAR JOINT STRENGTH (KN)					
	0	1	2	4	7.5	(weeks of Exposure)
4% ZrO ₂ sol 2% Amino silane 7% Silica	3.9	3.1	2.6	2.5	1.6	
Electrogalvanising	3.9	2.6	2.0	1.7	1.2	

EXAMPLE 26

The integrity of the pretreatment film on the aluminium surface was measured by immersing the pretreated coupon in acidified copper sulphate solution. The time taken for copper to electroplate on the aluminium surface was measured. The results are shown in Table 8.

TABLE 8

PRETREATMENT	COPPER DEPOSITION TIME (SEC)
untreated	36
1.5% Flame hydrolysed alumina (1.5g Al ₂ O ₃ /100 ml H ₂ O) [TYPE C sol]	60
2.5% Zirconia sol (1.1g ZrO ₂ /100ml H ₂ O) [TYPE A sol]	192

Longer copper deposition time (hence better corrosion protection) resulted from the Type A sol.

EXAMPLE 27

A pretreatment formulation consisting of 1% ZrO₂ sol, 0.8% amino silane and 4% silica prepared as described in Example 22 (formulation 1), was roller coated on aluminium foil, and heated to 200°C for 3 mins. The coated foil was immersed in liquid Nitrogen to cause embrittlement of the coating and then bent through 180°. Scanning electron microscopy revealed that the pretreatment layer did not delaminate under these conditions. The sol component formed a flexible skin adjacent to the metal surface and deformed with the metal. Cracking was observed in the pretreatment layer when a similar test was carried out on Alclad 4040 pretreated aluminium.

10 EXAMPLE 28

A pretreatment consisting of 1% ZrO₂ sol 0.5% aminosilane and 6% alumina (Example 22 formulation 3) was dehydrated by either spray drying or tray drying. The tray dried powder was redispersed in water and used to pretreat aluminium. The peel strength of the resultant metal:adherend joint was 55N. [The peel strength of a joint prepared with the original formulation, prior to dehydration and reconstitution was 74N].

EXAMPLE 29

A pretreatment formulation consisting of 3.1% ZrO₂ sol and 1% silane [N (β -aminoethyl) γ -aminopropyltrimethoxy silane] was roll coated on aluminium metal and dried at 80°C for 3 mins. Scanning electron microscopy revealed a smooth, featureless coating on the metal surface. The same pretreatment was also roller coated on phosphoric acid anodised metal. Scanning electron microscopy showed that the pretreatment coated the alumina whiskers while maintaining the open, porous topography. A cross section also revealed that the pretreatment had penetrated the anodic film and formed a dense layer adjacent to the metal surface.

A lacquer performance test on the pretreated panels gave the following results:

PRETREATMENT	TOTAL SCORE*	FEATHERING*
(A) Phosphoric acid anodising	25	4
(B) 3.1% ZrO ₂	26	2
1% silane		
(A) and (B)	18	1

(* Low score indicates good performance)

It should be noted that the phosphoric acid anodised surface was prepared two years ago. Electron microscopy showed that the surface topography remained unchanged after storage, but it is possible that surface contamination during storage is responsible for the poor lacquer adhesion results prior to pretreatment.

45 **Claims**

1. A method which comprises applying to a solid surface an aqueous composition comprising an inorganic hydrous oxide sol and curing the composition to form a protective coating on the surface.
2. A method as claimed in claim 1, wherein the inorganic sol is a hydrous metal oxide sol.
3. A method as claimed in claim 1 or claim 2, wherein the sol is a zirconia sol.
4. A method as claimed in any one of claims 1 to 3, wherein the surface is a metal surface.
5. A method as claimed in any one of claims 1 to 4, wherein the surface is of aluminium or titanium which has been pre-treated to form thereon an artificially applied oxide layer.
6. A method as claimed in any one of claims 1 to 5, wherein there is applied to the surface:
 - i) the aqueous composition comprising the inorganic sol to form a layer on the surface,
 - ii) a fluid which gels the sol on the surface,
 the applications being made sequentially in either order, and curing the resulting layer on the surface.

7. A method as claimed in any one of claims 1 to 6, wherein the aqueous composition and/or the fluid contains an adhesion promoter.

8. A method as claimed in any one of claims 1 to 7, wherein the adhesion promoter is selected from fluorozirconates, silane coupling agents, nitrilotrismethylene phosphonates, phosphates, and oxidizing agents for the surface.

9. A method as claimed in any one of claims 1 to 8, wherein the aqueous composition and/or the fluid contains from 1 to 300 g/l of a passenger powder.

10. A method as claimed in claim 9, wherein the passenger powder is selected from silica, alumina, zirconia and titania having an average particle size in the range 3 - 150 nm.

11. A method as claimed in any one of claims 1 to 10, wherein the aqueous composition contains a silane coupling agent as an adhesion promoter and a passenger powder.

12. A method as claimed in any one of claims 1 to 11, wherein the composition is cured by heating to a temperature of from 50°C to 400°C.

13. A method as claimed in any one of claims 1 to 12, including the additional step of applying an organic coating to the protective coating.

14. An aqueous composition for application to solid surfaces which compositions comprises:

- a) an inorganic hydrous oxide sol together with b) and/or c)
- b) an adhesion promoter
- c) from 1 to 300 g/l of a passenger powder having an average primary particle size in the range 3 - 250 nm, provided that the composition does not contain added hexavalent chromium or molybdenum.

15. A composition as claimed in claim 14, wherein component a) is a hydrous metal oxide sol of concentration 1 - 200 g/l metal oxide equivalent.

16. A composition as claimed in claim 14 or claim 15, wherein component b) is a silane coupling agent present at a concentration of 0.05% to 10% by volume on the volume of the sol.

17. A composition as claimed in any one of claims 14 to 16, comprising:

- a) a zirconia sol of concentration 1 - 200 g/l metal oxide equivalent,
- b) a silane coupling agent present at a concentration of 0.05% to 10% by volume on the volume of the sol, and
- c) a passenger powder selected from silica, alumina, zirconia and titania, having an average particle size in the range 3 - 150 nm, and present at a concentration of 5 - 150 g/l.

18. A particulate solid formed by drying the composition of any one of claims 14 to 17 and having the property of being re-dispersable in water to form the composition of any one of claims 14 to 17.