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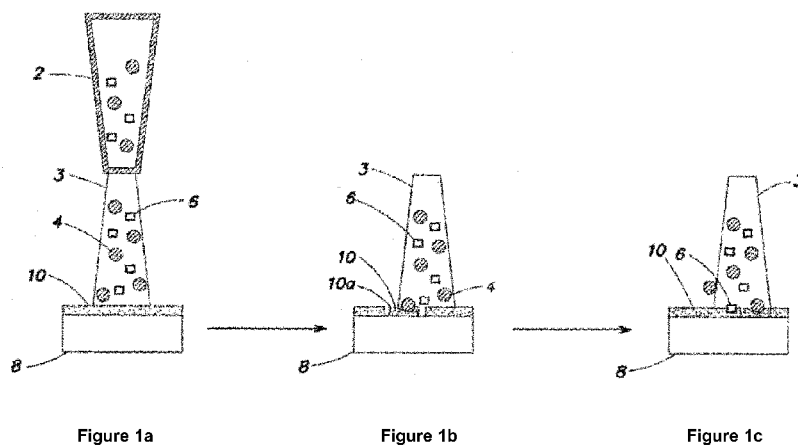
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(54) Title: METHOD FOR PRODUCING A CORROSION-INHIBITING OR ADHESION-PROMOTING COATING



(57) **Abstract:** A method of treating a substrate, the method comprising: delivering substantially simultaneously a first set of particles comprising a dopant and a second set of particles comprising an abrasive from at least one fluid jet to a surface of the substrate, to impregnate the surface of the substrate with the dopant; wherein the dopant comprises a corrosion-inhibiting or adhesion-promoting species, such as to form a corrosion-inhibiting or adhesion-promoting coating at or on the surface of the substrate. Also provided is an article comprising a substrate having a corrosion-inhibiting or adhesion-promoting coating, the said coating comprising particles of a corrosion-inhibiting or adhesion-promoting species that impregnate the surface of the substrate (e.g. as produced by the above method).

## METHOD FOR PRODUCING A CORROSION-INHIBITING OR ADHESION-PROMOTING COATING

### Field of the Invention

- 5 The present invention relates to surface treatment techniques in the field of materials science.

### Background to the Invention

- Abrasion may be defined as the action or process of scraping or grazing something, or of wearing something down by friction; the action or fact of becoming worn down in this way. The bombardment of metal surfaces with abrasive materials is finding an increasing number of technical applications in recent years. Techniques such as grit blasting, shot blasting, sand blasting, and micro abrasion fall under this category of surface treatment techniques. In each of these techniques, generally, an abrasive material, shot or grit, is mixed with a fluid and delivered at high velocity to impinge the surface to be treated. The technique used to deliver the abrasive material can be classified as wet or dry depending on the choice of fluid medium used to deliver the abrasive to the surface, usually water and air respectively. Alternatively, the abrasive can be propelled at the surface using a spinning wheel or paddle using a wheelblast machine. As the wheel turns, the abrasive particles are accelerated and directed toward the target where they impact and abrade as per standard fluid abrasion systems. These systems do not require any fluid or compressed gas to propel the particles at the surface. The generic term "abrasive bombardment" is used to refer to all such techniques in this specification. These techniques are different to shot peen techniques which bombard a surface with rounded particles to alter the stress level in the substrate or to induce a dimpled surface texture without producing significant material abrasion. (For the avoidance of any uncertainty, though, it will be appreciated that abrasive bombardment techniques can potentially alter the stress level in the surface of the substrate, as well as producing material abrasion.)

Applications of abrasive bombardment includes metal cutting, surface cleaning and the pre-treatment of surfaces to induce desirable texture (surface roughness) for the purposes of enhanced adhesion of further coating materials. (See Solomon et al., *Welding Research*, 2003. **October**: p. 278-287; Momber et al., *Tribology International*, 2002. **35**: p. 271-281; Arola et al., *J. Biomed. Mat. Res.*, 2000. **53**(5): p. 536-546; and Arola and Hall, *Machining Science and Technology*, 2004. **8**(2): p. 171-192.). An example of the latter is to be found in the biomedical sector where titanium implants are grit blasted with alumina or silica to achieve an optimum level of surface roughness that will maximize the adhesion of plasma sprayed hydroxyapatite (HA) coatings on the surface of the implants. HA coated implants are desirable because of the biomimetic properties of the apatite layer but an optimum bonding strength between the titanium surface and the apatite layer is also necessary.

It has been known for some time that during the bombardment of these surfaces some of the abrasive material becomes impregnated in the surface of the metal itself, which has generated some interest in these techniques as possible candidates for modifying surface chemistry in general. (See Arola et al. and Arola and Hall, *supra*). Again with reference to the biomedical sector one study has looked at shot blasting as a means of putting a hydroxyapatite layer directly on to a titanium surface in an effort to bypass the costly plasma spray process (Ishikawa, K., et al., *Blast coating method: new method of coating titanium surface with Hydroxyapatite at room temperature*. *J. Biomed. Mat. Res.*, 1997. **38**: p. 129-134). In this study, HA of an unspecified particle size distribution was used as the abrasive. However, given that the deposited layer of apatite could be removed with a benign washing regime it seems that a strong bond with the surface of the metal was not achieved.

Choi et al. (KR 2003-0078480) refer to the use of a single calcium phosphate particle as a grit blasting media for the purposes of embedding the grit in the surface of dental implants but particles in excess of 190  $\mu\text{m}$  are disclosed.

US Patent No. 6,502,442 refers to the use of sintered HA as the abrasive using water as the fluid medium. Some impregnation of the HA was achieved in this instance as the HA was thermally processed.

- 5 Muller et al. (US 2004/158330) disclosed blasting particles comprising calcium phosphate contained in a glassy matrix. Other disclosures (e.g., US Patent Nos. 4,752,457 and 6,210,715) describe methods for the manufacture of calcium phosphate micro-spheres usually comprising a polymer component and complex methods of manufacturing the same, but their effectiveness as blasting media was  
10 not elucidated.

The Rocatec™ system for the silicization of metallic and other surfaces also uses individual particles having multiple components. This technology is used extensively in the dental arena. In this instance an alumina particle having an  
15 outer adherent layer of silica is propelled at a pre-roughened surface and upon impact the local heat generated in the vicinity of the impact causes the shattered silica outer layer to become fused to the surface through a process referred to as ceramicization.

- 20 Bru-Magniez et al. (US Patent No. 6,431,958) have disclosed hard abrasive materials with multiple stratified layers for use in blasting abrasive bombardment techniques to modify surfaces. In this instance the purpose of the process was to embed or otherwise attach the stratified layer around the abrasive particles to the surface being treated. The outer layer comprises at least one polymer while the  
25 core ceramic material of choice is an oxide, carbide, nitride, or carbonitride.

The use of multiple stratified polymeric layers has been proposed. Lange et al. (US Patent No. 6,468,658) have disclosed a particle composed of a core base material and an outer adherent layer of titanium dioxide for blasting purposes.

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Further applications of abrasive bombardment for the purposes of surface modification are to be found in the biomedical sector such as for example the use of micro abrasion to clean the oxide slag from the struts of laser machined

coronary stents and the impregnation of the surfaces of pacemakers and defibrillators with silica to increase the adhesion of further polymer coatings to the device.

- 5 A commonality among these examples is the use of a single type of solid particle in the fluid stream. This may be a pre-treatment step in advance of subsequent coating.

US Patent No. 3,754,976 offers a different approach in which two separate  
10 particles are used. The patent describes a process for metal plating which comprises spraying a mixture of metallic powder and small peening particles at high velocity against a surface, said velocity being sufficient to impact and bond said metallic powder onto said surface to form a laminate layer of metal. The process is limited to a combination of a non-abrasive, shot peening particles and  
15 metallic powders. US Patent No. 4,552,784 offers a similar approach, wherein a stream of shot peening particles are combined with a stream of rapidly solidified metal powder particles such that upon impacting the substrate, the metal powder is deposited as a laminate layer upon the metal surface. No abrasive is used in this process and the deposition is limited to metal precursors. US Patent No.  
20 4,753,094 describes a process which comprises spraying a stream of molybdenum disulfide powder mixed with steel shot at a predetermined velocity against the substrate, the velocity being sufficient, when impacting the substrate, to bond minute plate-like particles of molybdenum disulfide to the substrate and form a friction reducing surface thereon. The process makes no mention of  
25 abrasive particles and the steel shot used is typically used in the non-abrasive shot peen process.

US Patent No. 8,119,183 and WO 2008/033867, in the name of EnBio Limited, disclose an alternate strategy wherein the abrasive blasting and coating  
30 deposition are carried out simultaneously by combining the flow of abrasive and flow of coating precursor (dopant) into a single step to modify the surface of a metal implant. The abrasive is used to remove the oxide layer and bind the dopant to the metal in a single step, thus providing a new method to alter the

metal surface of a medical and a range of biologically relevant dopants were described for this coating process. The dopant species are used to improve the biomedical properties of the surface of the device. No corrosion resistant dopants were considered, as the materials used to manufacture medical implants are naturally resistant to corrosion and do not require corrosion protective coatings.

#### *Corrosion-inhibiting coatings*

In areas of industrial application other than medical implants, however, a substrate may be susceptible to corrosion, due to the presence of corrosive species in the vicinity of the substrate (for example during use of the substrate, or during subsequent processing or storage of the substrate, etc.). There is therefore a desire to provide a corrosion-inhibiting surface treatment to such a substrate. In the present work the term "corrosion-inhibiting" should be interpreted broadly, to encompass treatments that reduce the susceptibility of the substrate to corrosion, as well as those which prevent corrosion altogether.

Two main types of corrosion-inhibiting surface treatments considered in the present work are conversion coatings and mechanically-bonded coatings.

#### *Conversion coatings*

Conversion coatings are routinely used to protect metal components in industries such as aerospace, marine, petrochemicals and many others. A conversion coating is a treatment of a metal substrate wherein at least part of the surface is converted into the coating with a chemical or electro-chemical process. Examples include chromate conversion coatings, phosphate conversion coatings and anodizing. The most common reasons for applying conversion coatings are to enhance corrosion protection, to change the surface colour, to increase the surface hardness or to deposit a primer layer on the surface to enhance adhesion of a subsequent layer. Chromate conversion coatings have dominated the corrosion coating market in a number of sectors, but these coatings are diminishing in popularity due to the negative environmental impact of the chromate conversion process, largely due to the toxicity of the hexavalent chromium used in

the coating process. This has led to a gradual increase in the significance of phosphate coatings, and particularly zinc phosphate coatings.

5 All of these coatings require a pre-treatment step and this frequently involves abrasively blasting the surface prior to coating. For example, phosphate conversion coating is a complex process that involves a significant number of steps and involves a multi-stage surface treatment strategy. Typically, the first step involves cleaning the surface. This can be accomplished by various methods including immersion in solvents, etching agents, acids, bases, degreasing agents  
10 and physical cleaning of the surface using ultrasonic tanks or physical abrasion, using techniques such as grit blasting. Many of these processes involve dangerous or toxic chemicals and are carried out at elevated temperatures. Following on from the cleaning step, the surface may be then further activated. This can be a physical activation using grit blasting or mechanical abrasion which  
15 disrupts the native oxide layer, roughens the surface and leaves active sites available for subsequent binding to the conversion coating during a subsequent step. Alternatively, the surface can be activated using chemical means. For example, pre-treating the surface with colloidal titanium compounds immediately prior to the application of the conversion coating is popular for zinc phosphate  
20 coatings. Other compounds like dilute solutions of cupric or nickel sulphates, oxalic acid and polyphosphonates help in increasing the number of initial nuclei formed during the subsequent phosphating step and these pre-treatments yield thin and compact phosphate coatings of fine-grained nature. The activation step can involve a combination of initial grit blasting followed by subsequent chemical  
25 activation.

Actual phosphate deposition is a standalone processing step and is typically carried out using wet chemical solutions. The substrate is usually immersed in a bath of chemicals. The composition of these baths vary from manufacturer to  
30 manufacturer, but all typically contain dilute phosphoric acid based solutions containing alkali metal/heavy metal ions in them alongside suitable accelerators. These baths are typically heated to enhance the rate of reaction and optimise the surface finish. The chemical concentrations of reactants and waste products

within the bath steadily alters as the chemical reactions proceed and the bath has to be rigorously monitored and adjusted to maintain optimum performance. For larger parts, the physical size of the component can make chemical baths prohibitively large, complex and difficult to control. For these substrates, a spray  
5 phosphating process is used. Although largely similar to the wet chemical bath method, the chemical solution is instead sprayed on to the metal surface and allowed to react.

After the phosphating step, the components are usually washed, dried and then  
10 sent for further processing which may include deposition of additional layers, sealants, passivation treatments or paints. The overall phosphating process is slow, complex, requires considerable thermal input and uses harsh, toxic chemicals.

15 Therefore, there remains a desire to produce a corrosion-inhibiting conversion coating in a manner that can be readily employed to treat both large and small components, is simple to use, and does not require a multi-step treatment process that uses large amounts of energy and harsh chemicals.

#### 20 *Mechanically-bonded coatings*

Turning now to mechanically-bonded coatings, these are coatings which are bonded to the underlying substrate by mechanical interlocking between the coating and the underlying substrate, rather than being formed as a consequence of the surface of the substrate undergoing a chemical or electro-chemical reaction.

25 To prepare a substrate surface to receive a coating that is to be mechanically bonded to the substrate, conventionally the surface of the substrate is subjected to a separate pre-treatment process, to roughen the surface of the substrate. This produces, on the microscopic scale, a large number of crevices, depressions or other regions of unevenness in the surface of the substrate, into which the  
30 subsequently-applied coating can interlock. Such a roughening process is typically performed by sandblasting, after which the roughened surface is then cleaned. The coating is then applied in a separate process, e.g. by spraying. The use of separate sandblasting, cleaning and spraying processes in this manner (i.e.



as a multi-stage process) is time consuming and there is a desire to make such a process more efficient.

*Adhesion-promoting coatings (including primer layers)*

5 Although the above discussion has primarily focused on the direct application of a corrosion-inhibiting coating to the surface of a substrate, it will be appreciated that similar issues may be faced when forming an adhesion-promoting coating on a substrate. The expressions “adhesion-promoting”, “adhesion-promoting coating” and the like, as used herein, refer to coatings which are applied to a substrate to  
10 enhance the adhesive character of the surface of the substrate – i.e. to enable, promote or improve the adhesion of the substrate to another material or article with which the coated substrate subsequently comes into contact; or to enable, promote or improve the adhesion of a subsequently-deposited layer to the substrate (the coating thereby serving as a primer layer in respect of the  
15 subsequently-deposited layer).

As those skilled in the art will appreciate, a primer layer is a coating that is formed on the surface of a substrate. A subsequent coating is then applied to the primer layer. The primer layer is selected so as to bond well to the substrate, and such  
20 that the subsequently-applied coating bonds well to the primer layer. Thus, the primer layer acts as an intermediate layer between the substrate and the subsequently-applied coating, with an overall effect of better bonding between the subsequently-applied coating and the substrate than would be achieved if the primer layer were not present.

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As with the corrosion-inhibiting coatings discussed above, an adhesion-promoting coating can be formed as a conversion coating or a mechanically-bonded coating on an underlying substrate. In either case, the problems discussed above in relation to conversion coatings and mechanically-bonded coatings (in the context  
30 of corrosion inhibition) remain equally applicable.

## Summary of the Invention

According to a first aspect of the present invention there is provided a method of treating a metal substrate, the method comprising: delivering substantially simultaneously a first set of particles comprising a dopant and a second set of particles comprising an abrasive from at least one fluid jet to a surface of the metal substrate, to impregnate the surface of the metal substrate with the dopant; wherein the dopant comprises a corrosion-inhibiting species such as to form a corrosion-inhibiting conversion coating at the surface of the metal substrate.

- 10 The expression “metal substrate” as used herein should be interpreted broadly, to encompass not only substrates made of substantially pure metals, or of alloys, but also substrates made of composite materials having a metallic component, such as metal matrix composites.
- 15 By virtue of this substantially-simultaneous delivery technique, the action of the abrasive particles on the surface of the metal substrate aids the impregnation of the corrosion-inhibiting dopant particles into the surface of the metal substrate. This provides a way of producing a corrosion-inhibiting conversion coating in a manner that can be readily employed to treat both large and small components, is
- 20 simple to use, and does not require a multi-step treatment process.

- Further benefits that may be obtained as a result of the substantially-simultaneous delivery of the abrasive particles with the corrosion-inhibiting dopant particles include work hardening the surface of the metal substrate, and/or inducing a compressive stress into the surface of the metal substrate – both of which aid in improving the resistance of the metal to stress corrosion cracking. Since these effects happen substantially simultaneously with the impregnation of the corrosion-inhibiting dopant species into the surface of the metal (which is also promoted by the action of the abrasive particles), it will be appreciated that the delivery of the abrasive particles together with the corrosion-inhibiting dopant particles provides a synergistic benefit in terms of improving the corrosion resistance of the treated metal. That is to say, a physical modification to the surface of the metal (namely work hardening and/or compressive stress induction) can be achieved together

with a chemical modification (namely the addition of the corrosion-inhibiting dopant species).

Preferably the corrosion-inhibiting species is chemically bonded to the substrate.

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According to a second aspect of the invention there is provided a method of treating a metal substrate, the method comprising: delivering substantially simultaneously a first set of particles comprising a dopant and a second set of particles comprising an abrasive from at least one fluid jet to a surface of the metal substrate, to impregnate the surface of the metal substrate with the dopant; wherein the dopant comprises a corrosion-inhibiting species that forms a mechanically-bonded corrosion-inhibiting coating on the surface of the metal substrate.

15 By virtue of this substantially-simultaneous delivery technique, the action of the abrasive particles on the surface of the metal substrate aids the impregnation of the corrosion-inhibiting dopant particles into the surface of the substrate, and also causes folds or twists to be produced at the interface between the substrate and the coating, thereby enhancing the degree of mechanical bonding between the substrate and the coating, and the overall bond strength. Such a process is particularly applicable to substrate materials on which a conversion coating cannot be formed, and provides a way of producing a corrosion-inhibiting coating in a manner that can be readily employed to treat both large and small components, is simple to use, and does not require a multi-step treatment process.

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With both the first and second aspects, preferably the nature of the coating is such that no laminate layer of the dopant results.

In practice, the method may further comprise removing a metal oxide from a surface of the metal substrate by abrasive blasting, thereby exposing the metal surface; and substantially simultaneously delivering the particles comprising the corrosion-inhibiting dopant from at least one fluid jet to the metal surface to impregnate the surface of the substrate with the dopant. The physical process of

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the abrasive particles impinging on the surface of the metallic material acts to remove the surface oxide and substantially simultaneously embeds the dopant particles into or onto the surface. In addition, the abrasive blasting process can alter the microstructure of the underlying metal, compacting the surface and imparting compressive forces into the metal. This surface compressive stress can also help to reduce stress corrosion cracking as it counteracts the tensile forces that are necessary for crack propagation.

The removal of the passivating metal oxide layer exposes a reactive metal underneath. When this is combined with the impact energy from the dopant particle hitting the surface and the energy dissipated by the abrasive particle impaction, sufficient energy can be released to chemically bond the coating to the substrate. Furthermore, the bond formed by the combination of abrasive and dopant can increase the adhesion and/or durability of the dopant material. The abrasive may also churn and twist the substrate surface such that the dopant is physically mixed into the surface and is not just present as an external surface layer.

Surprisingly, it has been found that the deposit contains very little evidence of the abrasive particle. Instead, the substrate surface appears to be preferentially doped with the corrosion-inhibiting material. The abrasive materials appear to bounce off the surface with minimal abrasive grit impregnating the surface. In general, over 90% of the deposit is made up of the corrosion resistant material and less than 10% is derived from the abrasive. In some cases over 99% of the deposit is made up of the corrosion resistant material and less than 1% is derived from the abrasive particles.

The layer of corrosion-inhibiting material may be used as a final surface finish which acts as a corrosion resistant layer. Alternatively, the corrosion-inhibiting material may be further covered with one or more additional coating layer(s) to enhance the corrosion resistance (and/or scratch resistance) of the surface. These one or more additional different layer(s) may be applied by spraying, painting, dipping, vapor deposition or any suitable method to apply the subsequent

layer(s). The corrosion-inhibiting material may act as a primer onto which these additional layer(s) are able to adhere, thereby enhancing the adhesion strength of the subsequent layer(s) to the substrate metal. Adjusting the abrasive properties, dopant properties or blast conditions can alter the surface topography and chemistry of the deposited layer of corrosion resistant material, thereby optimising the primer surface to deliver improved primer performance.

The layer of corrosion-inhibiting material may be deposited over a repaired area on a metal surface. In order to apply certain repairs, such as welding or brazing, it is necessary to remove all external coatings and oxide layers to leave a bare metal that can be worked upon. After this repair step is complete, the bare metal remains exposed and is susceptible to corrosion. The application of a corrosion resistant material cannot be easily accomplished using traditional deposition techniques as field repairs generally occur in situations where complex wet chemical deposition techniques cannot be employed. As such, the repaired regions often suffer from excessive corrosion and can fail again. A simple particle blasting process, as described herein, could be easily used in such a situation to apply a corrosion-inhibiting surface treatment that would protect the repaired region and extend the lifetime of the product.

The method disclosed herein offers a one step process which cleans and roughens the surface, while converting the native oxide layer into a corrosion resistant surface. This is accomplished without the use of thermal energy and does not require the use of harmful, toxic or corrosive chemicals. Advantageously, the process is not limited by the size of the substrate and can be readily applied to large-scale engineering components such as pipeline sections, wind turbine components, civil engineering structures, external walls, marine components, automotive body parts or other such large metallic components that routinely suffer from corrosion. In a specific application, the component is a tubular pipe and the coating is applied to the internal or external surface of the pipe. When applied to the internal surface of a pipe, the coating may reduce corrosion and also reduce friction when pumping liquids through the pipe.

In one embodiment, the dopant is delivered in a gaseous carrier fluid, such as nitrogen, hydrogen, argon, helium, air, ethylene oxide, and combinations thereof. In another embodiment, the dopant is delivered in a liquid carrier fluid. In one embodiment, the liquid is also an etching liquid (basic or acidic). In one  
5 embodiment, the dopant is delivered in an inert environment.

The corrosion-inhibiting dopant material may be a chromate, phosphate, polymer (e.g. thermoset or thermoplastic), oxide or a nitride. The dopant may be cerium oxide (ceria). In a preferred method, the coating is derived from a phosphate  
10 compound. The phosphate may comprise a corrosion-inhibiting transition metal phosphate, such as iron phosphate, manganese phosphate or zinc phosphate, or combinations thereof. As the phosphate is not deposited by an electrochemical process, a range of materials can be incorporated into the surface by modifying the starting dopant powder.

In one embodiment the abrasive has a suitable property chosen from at least one of size, shape, hardness, and density to break an oxide layer on the metal substrate. In one embodiment, the abrasive has a Mohs hardness ranging from 0.1 to 10, such as a Mohs hardness ranging from 1 to 10, or a Mohs hardness  
20 ranging from 5 to 10. In a preferred method, the abrasive has a Mohs hardness ranging from 7 to 10. In another embodiment, the abrasive has a particle size ranging from 0.1  $\mu\text{m}$  to 10000  $\mu\text{m}$ , such as a particle size ranging from 1  $\mu\text{m}$  to 5000  $\mu\text{m}$ , or a particle size ranging from 50  $\mu\text{m}$  to 500  $\mu\text{m}$ . In a preferred method, the particle size of the abrasive is from 10  $\mu\text{m}$  to 150  $\mu\text{m}$ .

Abrasive materials to be used in this method include but are not limited to shot or grit made from silica, sand, alumina, zirconia, zirconate, barium titanate, calcium titanate, sodium titanate, titanium oxide, glass, biocompatible glass, diamond, silicon carbide, boron carbide, dry ice, boron nitride, calcium phosphate, calcium  
30 carbonate, metallic powders, carbon fibre composites, polymeric composites, titanium, stainless steel, hardened steel, carbon steel chromium alloys or any combination thereof.

The abrasive bombardment can be used to work harden the surface and this can interact synergistically with the corrosion-inhibiting dopant to limit stress corrosion cracking. The degree of work hardening can be tailored by altering the abrasive properties. Altering the size, shape or chemistry of the abrasive can alter the effects on the substrate. While the surface is severely deformed and is chemically altered by the presence of the dopant, the layers underneath are also altered. While the dopant does not penetrate into this sub-surface zone, the bombardment process can alter the grain structure of the underlying metal. This zone can extend for 10 – 50 microns and the depth of this zone can be controlled by altering the particle size, hardness or velocity of the abrasive. Increasing the energy of the abrasive enhances the depth of the modification effect. The grains in this modified region may exhibit twinning. Twinning has previously been observed in shot peened metals. The formation of twins is promoted by a high strain rate, shock loading and relatively large grain size. Underneath this structurally modified layer lies the un-deformed substrate.

The pressure of the fluid jet will also be a factor in determining the impact energy of the abrasive. The abrasive and dopant(s) do not have to be delivered to the surface through the same jet. They could be in any number of separate jets as long as they deliver the solid components to the surface at the substantially the same time, e.g., prior to reformation of any oxide layer. This allows a large amount of flexibility in optimizing the invention towards a specific need. For large substrates, multiple nozzles may be used to deliver abrasives and dopants to multiple points on the surface simultaneously, thereby accelerating the overall treatment rate.

In one embodiment, the fluid jet is selected from wet blasters and abrasive water jet peening machines. In one embodiment, the at least one fluid jet operates at a pressure ranging from 0.5 to 100 bar, such as a pressure ranging from 1 to 30 bar, or a pressure ranging from 1 to 10 bar.

In another embodiment, the at least one fluid jet is selected from dry blasters, wheel abraders, grit blasters, sand blasters, and micro-blasters. In one embodiment, the at least one fluid jet operates at a pressure ranging from 0.5 to 100 bar, such as a pressure ranging from 1 to 30 bar, or a pressure ranging from 3 to 10 bar.

In other embodiments, blasting equipment can be used in conjunction with controlled motion such as CNC or robotic control. The blasting can be performed in an inert environment.

In one embodiment, the dopants and abrasives are contained in the same reservoir and are delivered to a surface from the same jet (nozzle). In another embodiment, the dopant is contained in one reservoir and abrasive contained in a separate reservoir, and multiple nozzles deliver the dopants and abrasives. The multiple nozzles can take the form of a jet within a jet, i.e., the particles from each jet bombard the surface at the same incident angle. In another embodiment, the multiple nozzles are spatially separated so as to bombard the surface at different incident angles yet hit the same spot on the surface simultaneously.

In one embodiment, the article to be treated is a metal, such as those metals chosen from pure metals, metal alloys, intermetallic compounds or mixtures thereof. Exemplary metals include iron, zinc, cadmium, tin, silver, titanium, titanium alloys (e.g., NiTi or nitinol), ferrous alloys, stainless steel and stainless steel alloys, carbon steel, carbon steel alloys, aluminum, aluminum alloys, nickel, nickel alloys, nickel titanium alloys, tantalum, tantalum alloys, niobium, niobium alloys, chromium, chromium alloys, cobalt, cobalt alloys, precious metals, and precious metal alloys.

One of ordinary skill in the art can appreciate the influence of machine parameters including jet velocity, operating pressure, venturi configuration, angle of incidence and surface to nozzle distances on the extent of impregnation of the dopant in the surface using these mixed media.



One of ordinary skill in the art can appreciate the effect of the size, shape, density and hardness of the abrasive material used on the extent of impregnation of the dopant in the surface using these mixed media.

- 5 One of ordinary skill in the art can appreciate the effect of the fluid stream itself, the blasting equipment using a gas medium (typically air), and the effects of using inert gases as a carrier fluid (e.g. N<sub>2</sub> or noble gases such as Ar and He) on the extent of impregnation of the dopant in the surface using these mixed media.
- 10 According to a third aspect of the invention there is provided a method of treating a substrate, the method comprising: delivering substantially simultaneously a first set of particles comprising a dopant and a second set of particles comprising an abrasive from at least one fluid jet to a surface of the substrate, to impregnate the surface of the substrate with the dopant; wherein the dopant comprises an
- 15 adhesion-promoting species such as to form an adhesion-promoting coating at or on the surface of the substrate.

The adhesion-promoting species may form a conversion coating at the surface of the substrate.

20

Further, the adhesion-promoting species may be chemically bonded to the substrate.

- Alternatively, the adhesion-promoting species may form a mechanically-bonded
- 25 adhesion-promoting coating on the surface of the substrate.

- As with the corrosion-inhibiting coatings discussed above, by virtue of the substantially-simultaneous delivery technique employed in the third aspect of the invention, the action of the abrasive particles on the surface of the substrate aids
- 30 the impregnation of the adhesion-promoting dopant particles into the surface of the substrate. This provides a way of producing (either as a conversion coating or as a mechanically-bonded layer) a well-bonded adhesion-promoting coating in a

manner that can be readily employed to treat both large and small components, is simple to use, and does not require a multi-step treatment process.

In certain embodiments the adhesion-promoting species forms a primer layer on the substrate, i.e. the adhesion-promoting species serves as a primer-forming species. Such a primer-forming species may comprise a fluoropolymer such as PTFE, a perfluoroalkoxy material such as Teflon, polyvinylidene fluoride, perfluoropolyether, a perfluorinated elastomer, or polyvinylfluoride. Alternatively, or in addition, the primer-forming species may comprise a silane, siloxane, acrylate, epoxy, hydrogen bonded silicon compound or material which contains one or more vinyl, peroxyester, peroxide, acetate or carboxylate functional group.

One or more subsequent layers may be applied to the primer layer, such as a scratch-inhibiting layer, a corrosion-inhibiting layer, an adhesive layer, a non-stick surface or a solid low-friction layer (e.g. a fluoropolymer such as PTFE).

Alternatively, rather than acting as a primer layer *per se*, the adhesion-promoting coating may be provided so as to improve the adhesion of the substrate to another material or article with which the coated substrate subsequently comes into contact. In such instances, the adhesion-promoting may comprise, for example, a silane, siloxane, acrylate, epoxy, hydrogen bonded silicon compound or material which contains one or more vinyl, peroxyester, peroxide, acetate or carboxylate functional group.

In relation to all the above aspects, preferably the second set of particles (i.e. the abrasive particles) have an average particle size in the range of 1  $\mu\text{m}$  to 150  $\mu\text{m}$ , more preferably an average particle size in the range of 10  $\mu\text{m}$  to 150  $\mu\text{m}$ , and particularly preferably an average particle in the range of 50  $\mu\text{m}$  to 150  $\mu\text{m}$ . The use of small abrasive particles of such dimensions gives rise to enhanced disruption of the surface of the substrate, thereby promoting penetration of the dopant particles into the substrate surface and intermixing of the dopant particles with the substrate surface.

Preferably the first set of particles (i.e. the dopant particles) have an average particle size in the range of 1  $\mu\text{m}$  to 100  $\mu\text{m}$ .

Preferably the ratio of the first set of particles to the second set of particles is between 20:80 and 80:20 by weight. Particularly preferably the ratio of the first set of particles to the second set of particles is between 40:60 and 60:40 by weight.

In certain embodiments the first and second sets of particles may be delivered without the use of a carrier fluid.

More generally, according to a fourth aspect of the invention there is provided a method of treating a substrate, the method comprising: delivering substantially simultaneously a first set of particles comprising a dopant and a second set of particles comprising an abrasive from at least one fluid jet to a surface of the substrate, to impregnate the surface of the substrate with the dopant; wherein the dopant comprises a corrosion-inhibiting or adhesion-promoting species, such as to form a corrosion-inhibiting or adhesion-promoting coating at or on the surface of the substrate.

According to a fifth aspect of the invention there is provided an article comprising a metal substrate having a corrosion-inhibiting conversion coating, the conversion coating comprising particles of a corrosion-inhibiting species that impregnate the surface of the metal substrate. In this context, impregnation may be taken to mean a process wherein the dopant is present within the top 20 microns of the metal surface and is intimately intermixed with the metal. The impregnated material may also extend onto or above the metal surface, but it is also to be found penetrating into the metal. The dopant material is not formed as a laminate layer that sits solely on top of the metal substrate.

The term "article" as used herein should be interpreted broadly, to encompass a component part of a larger product, as well as an overall product.

According to a sixth aspect of the invention there is provided an article comprising a metal substrate having a mechanically-bonded corrosion-inhibiting coating, the mechanically-bonded coating comprising particles of a corrosion-inhibiting species that impregnate the surface of the metal substrate.

5

According to a seventh aspect of the invention there is provided an article comprising a substrate having an adhesion-promoting coating thereon, the adhesion-promoting coating comprising particles of an adhesion-promoting species that impregnate the surface of the substrate.

10

According to an eighth aspect of the invention there is provided an article comprising a substrate having a corrosion-inhibiting or adhesion-promoting coating produced by a method in accordance with the first, second, third or fourth aspect of the invention.

15

### **Brief Description of the Drawings**

Embodiments of the invention will now be described, by way of example only, and with reference to the drawings in which:

20

Figures 1a, 1b and 1c schematically illustrate a process for treating a metal substrate;

Figures 2a, 2b and 2c are schematic diagrams of three different nozzle configurations to deliver abrasive particles and dopant particles to a surface;

Figure 3 is a schematic cross-sectional representation of a metal substrate having a corrosion-inhibiting conversion coating;

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Figure 4 is a schematic cross-sectional representation of a metal substrate having a corrosion-inhibiting conversion coating on which a second layer has been formed;

Figure 5 is a schematic cross-sectional representation of a substrate having an adhesion-promoting coating;

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Figure 6 is a schematic cross-sectional representation of a substrate having an adhesion-promoting coating serving as a primer layer, onto which a subsequent coating has been formed; and

Figure 7 presents the results of lap-shear strength testing following various surface treatments on titanium (in respect of Example 5 discussed below).

### **Detailed Description of Preferred Embodiments**

- 5 The present embodiments represent the best ways known to the applicants of putting the invention into practice. However, they are not the only ways in which this can be achieved.

#### *Overview of variants*

- 10 The present embodiments provide a method of treating a substrate, the method comprising: delivering substantially simultaneously a first set of particles comprising a dopant and a second set of particles comprising an abrasive from at least one fluid jet to a surface of the substrate, to impregnate the surface of the substrate with the dopant; wherein the dopant comprises a corrosion-inhibiting or  
15 adhesion-promoting species, such as to form a corrosion-inhibiting or adhesion-promoting coating at or on the surface of the substrate.

The action of the abrasive particles on the substrate causes a rough interface to be formed between the substrate material and the coating formed thereon.

- 20 Furthermore, the degree of intermixing between the substrate and dopant species is such that no laminate layer of the dopant results.

The present embodiments may be subdivided into three main variants.

- 25 In accordance with a first variant, certain embodiments provide a method of treating a metal substrate, the method comprising: delivering substantially simultaneously a first set of particles comprising a dopant and a second set of particles comprising an abrasive from at least one fluid jet to a surface of the metal substrate, to impregnate the surface of the metal substrate with the dopant;  
30 wherein the dopant comprises a corrosion-inhibiting species such as to form a corrosion-inhibiting conversion coating at the surface of the metal substrate.

In accordance with a second variant, other embodiments provide a method of treating a metal substrate, the method comprising: delivering substantially simultaneously a first set of particles comprising a dopant and a second set of particles comprising an abrasive from at least one fluid jet to a surface of the metal substrate, to impregnate the surface of the metal substrate with the dopant; wherein the dopant comprises a corrosion-inhibiting species that forms a mechanically-bonded corrosion-inhibiting coating on the surface of the metal substrate.

In accordance with a third variant, further embodiments provide a method of treating a substrate (which need not be a metal), the method comprising: delivering substantially simultaneously a first set of particles comprising a dopant and a second set of particles comprising an abrasive from at least one fluid jet to a surface of the substrate, to impregnate the surface of the substrate with the dopant; wherein the dopant comprises an adhesion-promoting species such as to form (e.g. by conversion coating or mechanical bonding) an adhesion-promoting coating at or on the surface of the substrate.

*Substantially simultaneous particle delivery method*

For the details of carrying the method of each of the first, second and third variants, the reader is initially referred to WO 2008/033867, which describes techniques for the substantially simultaneous deposition of first and second sets of particles. However, it should be noted that WO 2008/033867 does not describe the dopant comprising a corrosion-inhibiting species such as to form a corrosion-inhibiting conversion coating or a mechanically-bonded corrosion-inhibiting coating at or on the surface of the metal substrate (as per the present first and second variants). WO 2008/033867 also does not describe forming an adhesion-promoting coating at or on the surface of the substrate (as per the present third variant).

Naturally, as those skilled in the art will appreciate, the first and second sets of particles are different from one another (i.e. the dopant species is different from the abrasive).

*Embodiments which form a corrosion-inhibiting coating at or on the surface of the substrate (first and second variants)*

Embodiments of the present method are encompassed in but not limited to the  
5 schematic representation shown in Figures 1a, 1b and 1c.

Figure 1a schematically shows a fluid jet (nozzle) 2 that delivers a stream 3 comprising a set of abrasive particles 4 substantially simultaneously with a set of dopant particles 6. The dopant particles 6 comprise a corrosion-inhibiting species.  
10 Particle sets 4 and 6 bombard a surface 10 of a metal substrate 8, to impregnate the surface of the metal substrate with the corrosion-inhibiting dopant.

In accordance with the first variant, a chemical or electro-chemical reaction may take place between the dopant species and the substrate material, resulting in the  
15 formation of a corrosion-inhibiting conversion coating at the surface of the metal substrate 8. The energy required to initiate these reactions may be provided by the impact of both sets of particles on the surface. The abrasive particles may not necessarily partake directly in the chemical reaction, but their impact on the surface may provide the activation energy to initiate the conversion reaction.

20 Alternatively, in accordance with the second variant, a mechanically-bonded corrosion-inhibiting coating may be formed on the surface of the metal substrate, with some of the corrosion-inhibiting dopant particles mechanically interlocking with the surface of the substrate, the surface having been roughened by the action  
25 of the abrasive particles.

The formation of the corrosion-inhibiting coating may also involve a combination of both conversion coating and mechanical bonding of the dopant particles to the surface of the substrate.

30 With both the first and second variants, during the deposition process the dopant particles that have been deposited are subjected to ongoing bombardment by the abrasive particles, repeatedly hammering the dopant particles onto and into the

surface of the substrate, resulting in an intimate mixing of the substrate and dopant species and a high level of bonding and interlocking between the two, such that, at the corrosion-inhibiting coating, no laminate layer of the dopant results.

5 In the embodiment illustrated in Figures 1a, 1b and 1c, the surface 10 is a metal oxide layer. As a result of bombardment by the abrasive particles 4, the surface oxide layer is disrupted, and breaches in the oxide layer 10 result to expose a new surface 10a of substrate 8 (Figure 1b). In the case of a metal substrate, the newly exposed surface is a metal surface. As the particle stream 3 continues to impinge  
10 the substrate 8, the dopant particles 6 are integrated into the surface 10 of the substrate 8 (Figure 1c). Such disruption of the oxide layer, to produce a newly exposed surface of metal, is particularly applicable if a chemical or electro-chemical reaction is to take place between the dopant and substrate species, enabling the dopant species to react with the substrate metal (rather than the  
15 surface oxide layer). However, disruption of the oxide layer is also beneficial if the coating is to be mechanically bonded to the substrate 8.

In some embodiments, the blasting equipment can be used in conjunction with controlled motion such as CNC (computer numerical control) or robotic control.  
20 The blasting can be performed in an inert environment.

In one embodiment, the dopants and abrasives are contained in the same reservoir and are delivered to a surface from the same jet (nozzle). In another embodiment, the dopant is contained in one reservoir and abrasive contained in a  
25 separate reservoir, and multiple nozzles deliver the dopants and abrasives. The multiple nozzles can take the form of a jet within a jet, i.e., the particles from each jet bombard the surface at the same incident angle. In another embodiment, the multiple nozzles are spatially separated so as to bombard the surface at different incident angles yet hit the same spot on the surface simultaneously.

30

Figures 2a, 2b and 2c are schematic diagrams of three different nozzle configurations to deliver the dopants and abrasive to a surface: single nozzle (Figure 2a); multiple nozzles with dopants and abrasives delivered from separate



reservoirs where one nozzle is situated within another nozzle (Figure 2b); and multiple, separate nozzles with dopants and abrasives delivered from separate reservoirs (Figure 2c). More specifically, Figure 2a shows a single nozzle 20 for delivering a single stream 23 of abrasive particles 24 and corrosion-inhibiting dopant particles 26 to a substrate 28. Figure 2b shows that multiple nozzles with dopants and abrasives delivered from separate reservoirs can be used, with Figure 2b illustrating one nozzle 30 for delivering a stream 33 of abrasive particles 24 situated within another nozzle 40 for delivering a stream 43 of corrosion-inhibiting dopant particles 26, where streams 33 and 43 are coaxial. Multiple, separate nozzles with dopants and abrasives delivered from separate reservoirs can also be used, as indicated in Figure 2c, which shows nozzles 30 and 40, for delivering streams 33 and 43 of abrasive particles 24 and corrosion-inhibiting dopant particles 26, respectively.

The distance D between the nozzle(s) and the substrate surface can be in the range of 0.1 mm to 100 mm, such as a range of 0.1 mm to 50 mm, or a range of 0.1 mm to 20mm. The angle of the nozzle to the surface can range from 10 degrees to 90 degrees, such as a range of 30 degrees to 90 degrees, or a range of 70 to 90 degrees.

More than one type of dopant species can be used. It will readily be appreciated that where more than one type of dopant is used, the dopants may be delivered from a single nozzle, or each type may respectively be delivered from a separate nozzle.

As illustrated in Figure 3, the layer of corrosion-inhibiting material 52 may be used as a final surface finish which acts as a corrosion resistant layer for the substrate 8. As discussed above, such a corrosion resistant layer 52 may be formed as a conversion coating at the surface of the substrate 8, or as a layer that is mechanically bonded to the substrate 8.

Alternatively, as shown in Figure 4, the corrosion-inhibiting layer 52 may be further covered with one or more additional coating layer(s) 54 to enhance the corrosion

resistance (and/or scratch resistance) of the surface. These one or more layer(s) may be applied by spraying, painting, dipping, vapor deposition or any suitable method to apply the subsequent layer(s). The corrosion-inhibiting material 52 may act as a primer onto which these additional layer(s) 54 are able to adhere, thereby enhancing the adhesion strength of the subsequent layer(s) 54 to the substrate metal 8. Adjusting the abrasive properties, dopant properties or blast conditions can alter the surface topography and chemistry of the deposited layer of corrosion resistant material 52, thereby optimising the primer surface to deliver improved primer performance.

Applications of the above technique for forming a corrosion-inhibiting coating include (but are in no way limited to) providing corrosion protection for:

- large-scale engineering components such as pipeline sections
- wind turbine components
- civil engineering structures
- external walls
- marine components
- automotive body parts
- oil and gas industry components
- aerospace components

*Embodiments which form an adhesion-promoting coating at or on the surface of the substrate (third variant)*

As with the above-described method for the formation of a corrosion-inhibiting coating, embodiments which form an adhesion-promoting coating are also encompassed in but not limited to the schematic representation shown in Figures 1a, 1b and 1c, in this case with the dopant particles 6 comprising an adhesion-promoting species. Particle sets 4 and 6 bombard a surface 10 of a substrate 8, which in some embodiments may be metal, but in others may be a non-metal (e.g. a polymer or ceramic) or a composite material, so as to impregnate the surface of the substrate 8 with the adhesion-promoting species.

If the substrate 8 is metal then the surface 10 may again comprise a metal oxide layer. As a result of bombardment by the abrasive particles 4, the surface oxide layer is disrupted, and breaches in the oxide layer 10 result to expose a new surface 10a of substrate 8 (Figure 1b). For a metal substrate, the newly exposed surface is a metal surface. As the particle stream 3 continues to impinge the substrate 8, the adhesion-promoting dopant particles 6 are integrated into the surface 10 of the substrate 8 (Figure 1c). Such disruption of the oxide layer, to produce a newly exposed surface of metal, is particularly applicable if a chemical or electro-chemical reaction is to take place between the dopant and substrate species, enabling the dopant species to react with the substrate metal (rather than the surface oxide layer). However, disruption of the oxide layer is also beneficial if the adhesion-promoting coating is to be mechanically bonded to the substrate 8.

As with the above-described method, three different possible nozzle configurations are illustrated schematically in Figures 2a, 2b and 2c.

A chemical or electro-chemical reaction may take place between the adhesion-promoting species and the substrate material, resulting in the formation of an adhesion-promoting conversion coating at the surface of the substrate 8.

Alternatively, a mechanically-bonded adhesion-promoting coating may be formed on the surface of the substrate, with some of the adhesion-promoting dopant particles mechanically interlocking with the surface of the substrate, the surface having been roughened by the action of the abrasive particles.

The formation of the adhesion-promoting coating may also involve a combination of both conversion coating and mechanical bonding of the dopant particles to the surface of the substrate.

With the third variant, during the deposition process the dopant particles that have been deposited are subjected to ongoing bombardment by the abrasive particles, repeatedly hammering the dopant particles onto and into the surface of the substrate, resulting in an intimate mixing of the substrate and dopant species and

a high level of bonding and interlocking between the two, such that, at the adhesion-promoting coating, no laminate layer of the dopant results.

Figure 5 shows a schematic cross-sectional representation of a substrate 8 having an adhesion-promoting coating 56, formed either as a conversion coating at the surface of the substrate, or as a mechanically-bonded coating on the surface of the substrate.

Optionally, in certain embodiments, the adhesion-promoting coating 56 may be deposited in an uncured or semi-cured form, for curing in a separate step using heat, radiation, moisture, etc., prior to the application of any subsequent coating. Such curing may be performed in a localised manner (e.g. using localised infra-red curing).

The adhesion-promoting coating 56 may be provided so as to improve the adhesion of the substrate 8 to another material or article with which the coated substrate subsequently comes into contact. That is to say, the production of the adhesion-promoting coating 56 may be the only surface treatment process carried out on the substrate.

However, as shown in Figure 6, the adhesion-promoting coating 56 may alternatively serve as a primer layer, onto which a further coating 58 (or a plurality of subsequent coatings) may subsequently be applied. The coating 58 may be, for example, a scratch-inhibiting coating, or a corrosion-inhibiting coating (to inhibit corrosion of the underlying substrate 8), or a solid low-friction or non-stick coating such as polytetrafluoroethylene (PTFE), or an adhesive layer to enable the underlying substrate 8 to be adhesively bonded to another article. In other embodiments the coating 58 may comprise some other kind of fluoropolymer layer, a paint layer (e.g. epoxy paint), or a ceramic coating, etc. Subsequent fluoropolymer layers can also be applied to minimise the accumulation and deposition of unwanted scale, debris, asphaltenes, paraffins or debris which can impair the operation of the underlying substrate. For such fluoropolymer coatings, a fluoropolymer primer such as PTFE has been found to be especially beneficial

as it allows the thick fluoropolymer coating to be effectively adhered to the substrate underneath. This was unexpected, as the first layer of fluoropolymer which impregnated the substrate would be expected to act as a release layer that would minimise the adhesion of subsequent layers. In contrast, it has been found  
5 that the subsequent fluoropolymer coatings adhere to the primer layer of fluoropolymer and the adhesion of the subsequent layer is enhanced by the presence of the primer layer. This process can be further enhanced by heating the multi-layered structure such that the fluoropolymer layers are thermally coalesced. Such coatings have been found to be highly beneficial when applied  
10 to the inner surfaces of pipes where they decrease corrosion and reduce maintenance requirements.

Optionally, in certain embodiments, the subsequently-applied coating 58 may be deposited in an uncured or semi-cured form, for curing in a separate step using  
15 heat, radiation, moisture, etc. Such curing may be performed in a localised manner (e.g. using localised infra-red curing).

Applications of the above techniques for forming an adhesion-promoting coating or a primer layer include (but are in no way limited to):

- 20 • Improving the adhesion of protective coatings on inner and outer surfaces of pipes to minimise build up of scale or to minimise corrosion.
- Enhanced adhesion of glues, silicones and other adhesives to metal components for improved bonding strength.
- Improved adhesion of protective paints for use in marine, aerospace or  
25 industrial applications.
- Improved adhesion of anti-scratch coatings.
- Formation of “non-stick” coatings – for example on articles such as utensils, saucepans or other items (both domestic and industrial) used in the cooking of foodstuffs, to inhibit foodstuffs from sticking during cooking. For all such  
30 purposes the non-stick coating would be bonded to the substrate using a primer layer, and may comprise a fluoropolymer such as PTFE.

- Mould-release applications – i.e. to form a non-stick coating on the inner surface of a mould (the mould typically being made of metal), to facilitate, in use of the mould, the removal of a moulded article from the mould. The non-stick coating would be bonded to the mould surface using a primer layer, and may comprise a fluoropolymer such as PTFE. Moulds coated in such a manner have many possible applications, including for the manufacture of vehicle tyres, engineering components, consumer products, and so on.
- The treatment of surfaces of engineering components where a low coefficient of friction is required, by bonding a low-friction coating (comprising, for example, a fluoropolymer such as PTFE) to the surface of the engineering component using a primer layer.
- Bonding applications – i.e. to form an adhesive coating on a substrate to enhance the degree of bonding between the substrate and another material or article with which the coated substrate subsequently comes into contact. For example, metal wires may be treated with a bonding agent (the wire being the substrate in such a case) to promote the degree to which they will bond to rubber. Such wires may then used, for example, in the manufacture of vehicle tyres, the wires being encased within the rubber to provide reinforcement to the tyre.
- Improved bonding of metals to composites and plastics, more generally.

#### Examples of abrasive species

Abrasive species that may be used in any of the above variants of the present method (as a second set of particles, delivered substantially simultaneously with a first, different, set of particles comprising a dopant) include but are not limited to shot or grit made from silica, sand, alumina, zirconia, barium titanate, calcium titanate, sodium titanate, titanium oxide, glass, biocompatible glass, diamond, silicon carbide, boron carbide, dry ice, boron nitride, calcium phosphate, calcium carbonate, metallic powders, carbon fibre composites, polymeric composites, titanium, stainless steel, hardened steel, carbon steel chromium alloys or any combination thereof.

The abrasive particles preferably have a hardness of at least 7 on the Mohs scale.

The abrasive particles preferably have an average particle size (diameter) in the range of 1  $\mu\text{m}$  to 150  $\mu\text{m}$ , more preferably in the range of 10  $\mu\text{m}$  to 150  $\mu\text{m}$ , and particularly preferably in the range of 50  $\mu\text{m}$  to 150  $\mu\text{m}$ . The use of small abrasive particles of such dimensions gives rise to enhanced disruption of the surface of the substrate, thereby promoting penetration of the dopant particles into the substrate surface and intermixing of the dopant particles with the substrate surface. Thus, the dopant species is impregnated into the substrate such that no laminate layer of the dopant results.

#### Examples of corrosion-inhibiting dopant species

With regard to the first and second variants described above, corrosion-inhibiting dopant species that may be used in the present method (as a first set of particles, different from the second) include but are not limited to a chromate, phosphate, polymer (e.g. a thermoset or a thermoplastic), oxide or a nitride. For example, the dopant may be ceria. In a preferred method, the coating is derived from a phosphate compound. The phosphate may comprise iron phosphate, manganese phosphate, zinc phosphate or combinations thereof. As the phosphate is not deposited by an electrochemical process, a range of materials can be incorporated into the surface by modifying the starting dopant powder.

It is particularly noteworthy that the corrosion-inhibiting dopant species need not be a metal or a metal salt, which are inherently sacrificial in nature. Polymer based dopants may be deposited which form a stable deposit on the substrate surface and prevent corrosion by inhibiting the build-up of corrosive materials on the surface or by physically isolating the corrosive species from the underlying substrate. Fluoropolymer, acrylate, acetate and epoxy based layers may all perform this function.

The dopant particles preferably have an average particle size (diameter) in the range of 1  $\mu\text{m}$  to 100  $\mu\text{m}$ .

Preferably the ratio of the dopant particles to the abrasive particles is between 20:80 and 80:20 by weight, and particularly preferably is between 40:60 and 60:40 by weight.

5

#### Examples of adhesion-promoting dopant species

With regard to the third variant described above, adhesion-promoting dopant species that may be used in the present method (as a first set of particles, different from the second) include but are not limited to fluoropolymers such as PTFE, perfluoroalkoxy materials such as Teflon, polyvinylidene fluoride, perfluoropolyethers, perfluorinated elastomers, polyvinylfluoride. They may also include silanes, siloxanes, acrylates, epoxys, hydrogen bonded silicon compounds or materials which contain one or more vinyl, peroxyester, peroxide, acetate or carboxylate functional group.

15

In particular examples, when forming an adhesion-promoting coating to serve as a primer layer for a polymer-based subsequent layer, the primer layer may be composed of the same materials as present within the subsequent layer. PTFE or other fluoropolymers may be used as primer-forming dopant species for the improved adhesion of subsequent fluoropolymer layers.

20

The dopant particles preferably have an average particle size (diameter) in the range of 1  $\mu\text{m}$  to 100  $\mu\text{m}$ .

Preferably the ratio of the dopant particles to the abrasive particles is between 20:80 and 80:20 by weight, and particularly preferably is between 40:60 and 60:40 by weight.

25

#### Examples

The following examples demonstrate the use and efficacy of the above method in forming corrosion-inhibiting coatings and adhesion-promoting coatings, including as primer layers.

30



**Example 1 – Deposition of Zinc Phosphate on a range of metal substrates (Aluminium, Copper, Grade 2 and 5 Titanium, Hastelloy, Inconel, Magnesium, Mild Steel, Stainless Steel (316))**

A series of metal substrates were obtained, made respectively of Aluminium, Copper, Grade 2 and 5 Titanium, Hastelloy, Inconel, Magnesium, Mild Steel and Stainless Steel (316). Zinc phosphate powder (< 5 microns average particle size) was mixed in equal volumetric proportions with alumina grit (100 micron average particle size) and then loaded into an Accuflow powder feeder. The powder was fed from there to a grit blast nozzle which was moved over the surface of the metal substrates and the powder was blasted at the surface at a pressure of 75 psi. Following blasting, the substrates were cleaned with compressed air to remove loose powder. All treated samples were visibly noted to have significant levels of zinc phosphate deposited on the surface. Surface characterisation was carried out using SEM and EDX analysis. EDX was used to determine the concentration of the coating by measuring and summing the Zn and P concentrations. There appeared to be a moderate coverage of zinc phosphate (> 30%) on all of the surfaces tested, confirming that the abrasive blasting process could effectively deposit a corrosion-inhibiting material. Examination of the deposited corrosion-inhibiting material suggested that it was formed by a combination of both a conversion process and mechanical bonding. Surface oxide is removed and so the zinc phosphate bonded to the surface as per conversion coatings, but some mechanical interlock is also seen, as a result of the bombardment process.

**Example 2 – Corrosion protection of mild steel**

Mild steel coupons and buttons were blasted with a mixture of zinc phosphate powder and alumina grit. Following deposition, the samples were analysed using EDX and both types of treated samples were found to have approximately 40% zinc phosphate present on the surface. The coated samples were then immersed in a 3.5% w/w NaCl solution. Untreated mild steel coupons and buttons were used as controls. After 72 hours, the untreated steel samples were visibly discoloured and the sample containers had a significant deposit of brown sediment which had settled to the bottom of the jar. The zinc phosphate treated samples showed no visible changes from their initial condition. There was no

evidence of any deposit, any discolouration or any other visible signs of corrosion. The test was continued until day 7, with the untreated samples continuing to degrade while the zinc phosphate blasted samples remained largely unchanged, thereby confirming the protective corrosion-inhibiting properties of the abrasive blasting treatment.

### **Example 3 – Primer for epoxy paint**

Mild Steel (Grade SAE 1008) was used for all samples. The following surface treatments were then applied to a number of samples:

- Untreated Blank sample (i.e. as-received)
- Grit Blasted (to Sa 2½ standard as per ISO 8501-1)
- Iron Phosphate (from Q-Panel – Henkel Bonderite M-FE 1000)
- Zinc Plated ('Tri-eco Zinc' procured from Meath Metal, Ireland)
- Commercial dry Zinc Phosphate Primer (manufactured by Johnstones)
- A Zinc Phosphate produced by blasting the metal with dry zinc phosphate powder (supplied by Delaphos) and 100 micron alumina. The two powers were premixed and then blasted at the surface through a De Laval nozzle at a pressure of 75 psi.

Each component was then coated with a SP320 two-part epoxy laminating paint procured from [www.UnionChandlery.ie](http://www.UnionChandlery.ie). This particular paint gave a clear coat to allow observation of the rust/corrosion growth from the introduced scratch.

Corrosion testing was carried out using a neutral salt fog cabinet as per ISO 9227.

A 'T' scribe was introduced to each sample using a carbide tip as per ISO 18782. Throughout the course of the experiment, each sample was removed periodically and photographed to log the growth of corrosion from the scratch. The samples were cleaned in deionised water to remove excess rust/corrosion on top of the sample prior to taking the photograph. The width/growth of the corrosion from the scratch was measured using the freely available imageJ software. Each coupon was removed from the salt fog cabinet at set intervals over a period of 56 days.

The width of the corrosion was measured using the imageJ software. A steel ruler was used to calibrate the scale.

Somewhat surprisingly, the 'Iron Phosphate' and 'Zinc Plated' samples performed quite poorly. In particular, the Zinc Plated sample exhibited significant delamination of the epoxy paint after 28 days and almost complete catastrophic failure after 56 days.

The Blank & Grit-Blasted coupons initially appeared to perform quite well and produced results that appeared superficially identical to the zinc phosphate coatings. However, when sectioned and examined in detail, it was evident that the depth of corrosion was much greater for these samples than for either of the zinc phosphate treatments. Both zinc phosphate treatments were noticeably better than the other commercial treatments. The blasted zinc phosphate tie-layer was very close in performance to that of the commercial Dry Zinc Phosphate primer (which utilised a noticeably thicker coating).

#### **Example 4 – Primer for fluoropolymer adhesion**

Four 3"x5" mild steel Q-panels were pre-treated with an abrasive blasting process as follows:

(i) Two were blasted with a mixture of 100 micron alumina and PTFE (Zonyl MP 1300) using a 80:20 mix by weight and a blasting pressure of 40 psi and a stand-off distance of 30 mm.

(ii) The other two were blasted with alumina only using the same conditions.

All samples were then washed in deionised water, dried with compressed air and then given a subsequent coating of PTFE fluoropolymer. The PTFE was sprayed at 2 psi and from 150 mm stand-off. To get a thick coating, three passes over the surface were required. All samples were then heated to 400°C in a carbolite furnace and then air cooled.

Adhesion testing was then carried out using a modified version of ISO 2409.

This aggressive version of ISO 2409 used a higher 'tack' tape (tesa 4613) and repeated tape pulls due to the poor adhesion between standard scotch tape and the PTFE coating. Prior to cutting, samples were boiled in DIW for 20 mins and then thoroughly dried and cooled. Cutting was carried out as per ISO 2409 with a multi-blade cutter with 2 mm spacing. Four separate areas were tested for each coating, and the tape pull was repeated 4 times at each test area. The ISO classification was followed, whereby samples that were undamaged by the tape test were rated 0, surfaces with less than 5% detachment were rated 1, surfaces with between 5 and 15% detachment were rated 2 and so on up until level 5.

After one tape test, samples prepared using the abrasively blasted pre-treatment yielded a value of 1, while the samples that were blasted with both abrasive and PTFE showed no effects and were therefore classified as 0. After four tape tests on the same area, the abrasively blasted samples were classified at level 2 to level 4, while the samples blasted with both abrasive and PTFE remained at classification 0 or 1, indicating significantly enhanced adhesion due to the PTFE primer.

Following this, samples were sectioned, mounted and polished, and viewed with a light microscope. Coating thickness was measured at 5 points on each sample at 10x magnification, and was consistent between the two coatings with both producing a thickness of 43 microns. No interface was visible between the PTFE primer layer and the top-coat, indicating they were completely fused.

#### **Example 5 – Improved bonding of adhesive to metal components**

The substrate in this case was grade V titanium. Five different surface treatments were then subjected to adhesion testing. These consisted of

- (i) Untreated titanium, henceforth called Blank.
- (ii) A grit blasted titanium surface produced by abrasively blasting the titanium with 50 micron alumina.
- (iii) A commercial Aerospace Primer. This consisted of Chromic Acid Anodized (CAA) surface followed by Cytec BR127 sol-gel primer. This will be referred to as 'CAA+Primer'.

- (iv) A surface produced by blasting titanium with a mixture of alumina and a Thermoset epoxy LT3366 from Huntsman (referred to as 'Epoxy')
- (v) A surface produced by blasting titanium with a mixture of alumina and Zinc Phosphate powder (Heubach ZP10)

5

All samples were then bonded to a carbon fibre reinforced plastic (CFRP). The CFRP was Hexcel 8552/5H which was prepared for bonding using a wet peel ply (Henkel Hysol EA9895). The adhesive was Cytec FM300 epoxy film adhesive (0.03gsm weight) which was cured at 177 C for 1 hour at a pressure of 45 psi.

10

Once the adhesive had fully cured, the samples were cooled to room temperature and then subjected to lap-shear testing, which was conducted in accordance with ISO 2243-1. The specimens were 25mm wide with a 12.5mm adhesive overlap. The lap-shear strength was calculated by dividing the force at failure by the overlap area. Four repetitions were performed for each surface treatment.

15

The results of these tests are shown in Figure 7. All of the surface treatments outperformed the untreated blank. Simple roughening with alumina abrasive was sufficient to increase the adhesion significantly, but both the untreated and grit-blasted joint systems resulted in interfacial failure. However, the deposition of a chemical primer was far more successful and all three chemical primers exhibited cohesive failure modes. Both the zinc phosphate and epoxy dopants significantly enhanced the adhesion of the joint and matched the performance of the commercial aerospace primer. It should be noted that the abrasive blasting methods were able to achieve this level of performance without the use of toxic chromate conversion coatings or the use of aggressive wet chemical primers.

20

25

#### Example areas of industrial application

The present method has potential application across a wide range of industries, including but not limited to: large-scale engineering components such as pipeline sections; wind turbine components; civil engineering structures; external walls; marine components; automotive body parts; oil and gas industry components; and aerospace components.

30

**CLAIMS**

1. A method of treating a metal substrate, the method comprising:

delivering substantially simultaneously a first set of particles comprising a  
5 dopant and a second set of particles comprising an abrasive from at least one fluid  
jet to a surface of the metal substrate, to impregnate the surface of the metal  
substrate with the dopant;

wherein the dopant comprises a corrosion-inhibiting species such as to  
form a corrosion-inhibiting conversion coating at the surface of the metal  
10 substrate.

2. A method as claimed in claim 1, wherein the corrosion-inhibiting species is  
chemically bonded to the substrate.

15 3. A method of treating a metal substrate, the method comprising:

delivering substantially simultaneously a first set of particles comprising a  
dopant and a second set of particles comprising an abrasive from at least one fluid  
jet to a surface of the metal substrate, to impregnate the surface of the metal  
substrate with the dopant;

20 wherein the dopant comprises a corrosion-inhibiting species that forms a  
mechanically-bonded corrosion-inhibiting coating on the surface of the metal  
substrate.

4. A method as claimed in any preceding claim, wherein the nature of the  
25 corrosion-inhibiting coating is such that no laminate layer of the dopant results.

5. A method as claimed in any preceding claim, wherein the method further  
comprises removing a metal oxide from the surface of the metal substrate to  
expose a metal surface, by abrasively blasting the metal oxide with the second set  
30 of particles substantially simultaneously with the delivery of the first set of  
particles.

6. A method as claimed in any preceding claim, wherein no pre-treatment process is performed before delivering the first and second sets of particles.

7. A method as claimed in any preceding claim, wherein the corrosion-inhibiting coating forms a first layer, and the method further comprises applying a second layer to the first layer.

8. A method as claimed in claim 7, wherein the first layer acts as a primer to enhance adhesion of the second layer.

9. A method as claimed in claim 7 or claim 8, wherein the second layer is a scratch-inhibiting layer.

10. A method as claimed in any of claims 7 to 9, wherein the second layer is a further corrosion-inhibiting layer.

11. A method as claimed in any preceding claim, wherein the corrosion-inhibiting species comprises a chromate, phosphate, polymer, oxide or a nitride.

12. A method as claimed in claim 11, wherein the corrosion-inhibiting species comprises a transition metal phosphate.

13. A method as claimed in claim 12, wherein the corrosion-inhibiting species comprises iron phosphate, manganese phosphate or zinc phosphate, or a combination thereof.

14. A method as claimed in claim 11, wherein the corrosion-inhibiting species comprises cerium oxide.

15. A method of treating a substrate, the method comprising:  
delivering substantially simultaneously a first set of particles comprising a dopant and a second set of particles comprising an abrasive from at least one fluid

jet to a surface of the substrate, to impregnate the surface of the substrate with the dopant;

wherein the dopant comprises an adhesion-promoting species such as to form an adhesion-promoting coating at or on the surface of the substrate.

5

16. A method as claimed in claim 15, wherein the adhesion-promoting species forms a conversion coating at the surface of the substrate.

17. A method as claimed in claim 16, wherein the adhesion-promoting species  
10 is chemically bonded to the substrate.

18. A method as claimed in claim 15, wherein the adhesion-promoting species forms a mechanically-bonded adhesion-promoting coating on the surface of the substrate.

15

19. A method as claimed in any of claims 15 to 18, wherein no pre-treatment process is performed before delivering the first and second sets of particles.

20. A method as claimed in any of claims 15 to 19, wherein the adhesion-  
20 promoting species forms a primer layer on the substrate.

21. A method as claimed in claim 20, wherein the adhesion-promoting species comprises a fluoropolymer such as PTFE, a perfluoroalkoxy material such as Teflon, polyvinylidene fluoride, perfluoropolyether, a perfluorinated elastomer, or  
25 polyvinylfluoride.

22. A method as claimed in claim 20 or claim 21, wherein the adhesion-promoting species comprises a silane, siloxane, acrylate, epoxy, hydrogen bonded silicon compound or material which contains one or more vinyl, peroxyester, peroxide, acetate or carboxylate functional group.  
30



23. A method as claimed in any of claims 20 to 22, wherein the primer layer forms a first layer, and the method further comprises applying a second layer to the first layer.

5 24. A method as claimed in claim 23, wherein the second layer is a scratch-inhibiting layer.

25. A method as claimed in claim 23, wherein the second layer is a corrosion-inhibiting layer.

10

26. A method as claimed in claim 23, wherein the second layer is an adhesive layer.

15

27. A method as claimed in claim 23, wherein the second layer is a solid low-friction layer.

28. A method as claimed in claim 23, wherein the second layer is a non-stick surface.

20

29. A method as claimed in any of claims 15 to 19, wherein the adhesion-promoting species comprises: a silane, siloxane, acrylate, epoxy, hydrogen bonded silicon compound or material which contains one or more vinyl, peroxyester, peroxide, acetate or carboxylate functional group.

25

30. A method as claimed in any of claims 15 to 29, wherein the nature of the adhesion-promoting coating is such that no laminate layer of the dopant results.

30

31. A method as claimed in any of claims 15 to 30, wherein the method further comprises removing a metal oxide from the surface of the substrate to expose a metal surface, by abrasively blasting the metal oxide with the second set of particles substantially simultaneously with the delivery of the first set of particles.

32. A method as claimed in any preceding claim, wherein the second set of particles have an average particle size in the range of 1  $\mu\text{m}$  to 150  $\mu\text{m}$ .

33. A method as claimed in claim 32, wherein the second set of particles have  
5 an average particle size in the range of 10  $\mu\text{m}$  to 150  $\mu\text{m}$ .

34. A method as claimed in claim 33, wherein the second set of particles have an average particle size in the range of 50  $\mu\text{m}$  to 150  $\mu\text{m}$ .

10 35. A method as claimed in any preceding claim, wherein the first set of particles have an average particle size in the range of 1  $\mu\text{m}$  to 100  $\mu\text{m}$ .

36. A method as claimed in any preceding claim, wherein the ratio of the first set of particles to the second set of particles is between 20:80 and 80:20 by  
15 weight.

37. A method as claimed in claim 36, wherein the ratio of the first set of particles to the second set of particles is between 40:60 and 60:40 by weight.

20 38. A method as claimed in any preceding claim, further comprising work hardening the surface of the metal substrate through the delivery of the second set of particles.

39. A method as claimed in any preceding claim, further comprising inducing a  
25 compressive stress into the surface of the metal substrate through the delivery of the second set of particles.

40. A method as claimed in any preceding claim, wherein the first and second sets of particles are delivered without the use of a carrier fluid.

30

41. A method of treating a substrate, the method comprising:  
delivering substantially simultaneously a first set of particles comprising a dopant and a second set of particles comprising an abrasive from at least one fluid

jet to a surface of the substrate, to impregnate the surface of the substrate with the dopant;

wherein the dopant comprises a corrosion-inhibiting or adhesion-promoting species, such as to form a corrosion-inhibiting or adhesion-promoting coating at or on the surface of the substrate.

42. An article comprising a metal substrate having a corrosion-inhibiting conversion coating, the conversion coating comprising particles of a corrosion-inhibiting species that impregnate the surface of the metal substrate.

43. An article as claimed in claim 42, wherein the corrosion-inhibiting species is chemically bonded to the substrate.

44. An article comprising a metal substrate having a mechanically-bonded corrosion-inhibiting coating, the mechanically-bonded coating comprising particles of a corrosion-inhibiting species that impregnate the surface of the metal substrate.

45. An article as claimed in any of claims 42 to 44, having no laminate layer of the corrosion-inhibiting species.

46. An article as claimed in any of claims 42 to 45, wherein the corrosion-inhibiting coating forms a first layer, the article further comprising a second layer disposed on the first layer.

47. An article as claimed in claim 46, wherein the first layer acts as a primer to enhance adhesion of the second layer.

48. An article as claimed in claim 46 or claim 47, wherein the second layer is a scratch-inhibiting layer.

49. An article as claimed in any of claims 46 to 48, wherein the second layer is a further corrosion-inhibiting layer.

50. An article as claimed in any of claims 42 to 49, wherein the corrosion-inhibiting species comprises a chromate, phosphate, polymer, oxide or a nitride transition metal phosphate.

5

51. An article as claimed in claim 50, wherein the corrosion-inhibiting species comprises a transition metal phosphate.

10

52. An article as claimed in claim 51, wherein the corrosion-inhibiting species comprises iron phosphate, manganese phosphate or zinc phosphate, or a combination thereof.

15

53. An article as claimed in claim 50, wherein the corrosion-inhibiting species comprises cerium oxide.

54. An article comprising a substrate having an adhesion-promoting coating thereon, the adhesion-promoting coating comprising particles of an adhesion-promoting species that impregnate the surface of the substrate.

20

55. An article as claimed in claim 54, wherein the adhesion-promoting species is chemically bonded to the substrate.

56. An article as claimed in claim 54, wherein the adhesion-promoting species is mechanically bonded to the substrate.

25

57. An article as claimed in any of claims 54 to 56, having no laminate layer of the adhesion-promoting species.

30

58. An article as claimed in any of claims 54 to 57, wherein the adhesion-promoting coating serves as a primer layer on the substrate.

59. An article as claimed in claim 58, wherein the adhesion-promoting species comprises a fluoropolymer such as PTFE, a perfluoroalkoxy material such as

Teflon, polyvinylidene fluoride, perfluoropolyether, a perfluorinated elastomer, or polyvinylfluoride.

60. An article as claimed in claim 58 or claim 59, wherein the adhesion-promoting species comprises a silane, siloxane, acrylate, epoxy, hydrogen bonded silicon compound or material which contains one or more vinyl, peroxyester, peroxide, acetate or carboxylate functional group.

61. An article as claimed in any of claims 58 to 60, wherein the primer layer forms a first layer, the article further comprising a second layer disposed on the first layer.

62. An article as claimed in claim 61, wherein the second layer is a scratch-inhibiting layer.

63. An article as claimed in claim 61, wherein the second layer is a corrosion-inhibiting layer.

64. An article as claimed in claim 61, wherein the second layer is an adhesive layer.

65. An article as claimed in claim 61, wherein the second layer is a solid low-friction layer.

66. An article as claimed in claim 61, wherein the second layer is a non-stick surface.

67. An article as claimed in any of claims 54 to 57, wherein the adhesion-promoting species comprises: a silane, siloxane, acrylate, epoxy, hydrogen bonded silicon compound or material which contains one or more vinyl, peroxyester, peroxide, acetate or carboxylate functional group.

68. An article as claimed in any of claims 42 to 67, wherein the substrate is metal, and the microstructure of the surface of the metal substrate exhibits work hardening.

5 69. An article as claimed in any of claims 42 to 68, wherein the surface of the substrate is under an intrinsic compressive stress.

70. An article comprising a substrate having a corrosion-inhibiting or adhesion-promoting coating produced by a method as claimed in any of claims 1 to 41.

10

71. An article as claimed in any of claims 42 to 70, being at least a part of:  
a large-scale engineering component such as a pipeline section;  
a wind turbine component;  
a civil engineering structure;  
15 an external wall;  
a marine component;  
an automotive body part;  
an oil or gas industry component; or  
an aerospace component.

20

72. A method of treating a substrate substantially as herein described with reference to and as illustrated in any combination of the accompanying drawings.

25

73. An article comprising a substrate having a corrosion-inhibiting or adhesion-promoting coating substantially as herein described with reference to and as illustrated in any combination of the accompanying drawings.

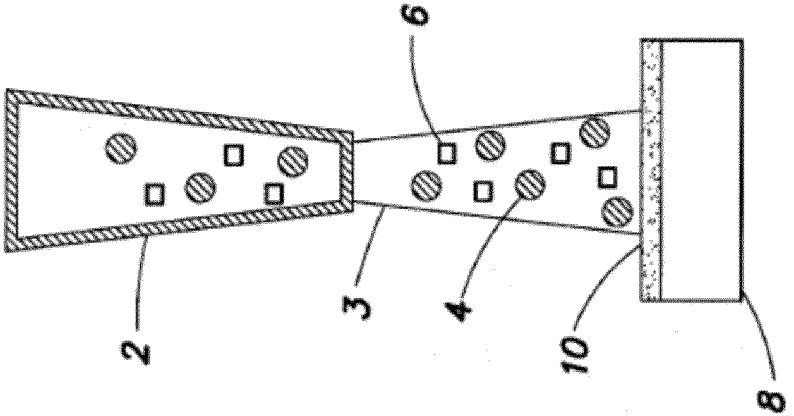


Figure 1a

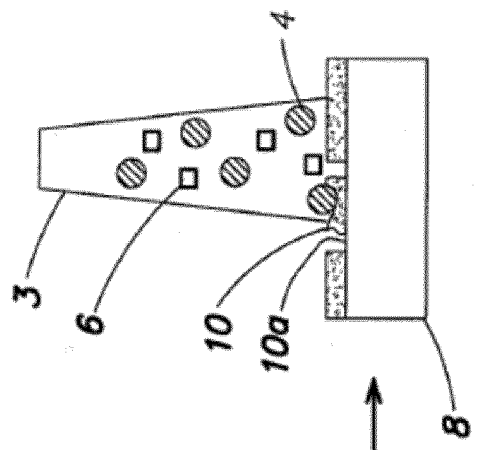


Figure 1b

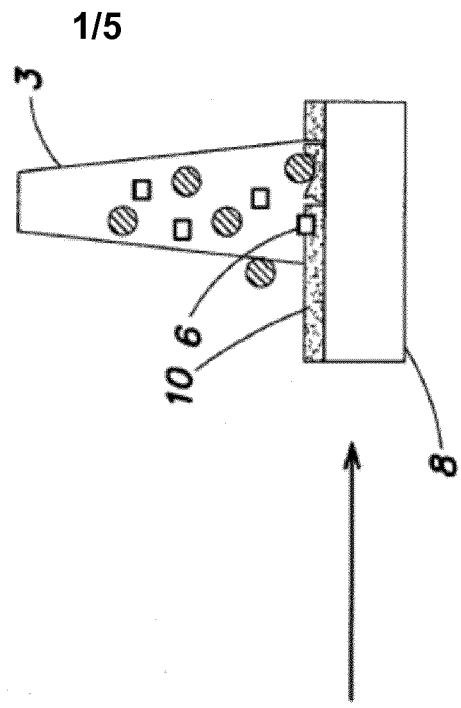


Figure 1c

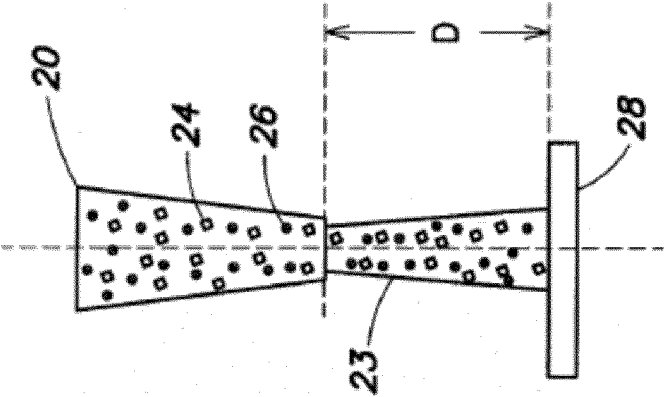


Figure 2a

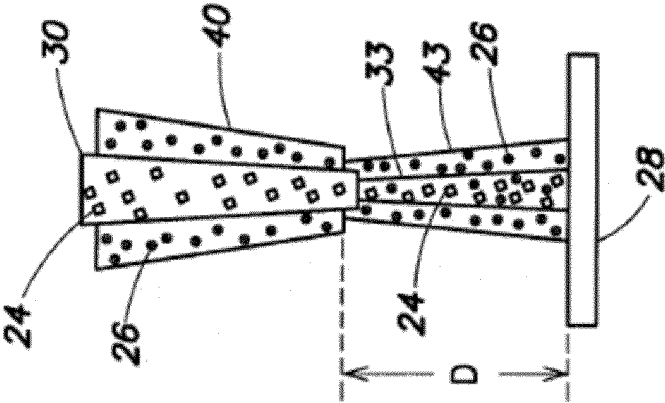


Figure 2b

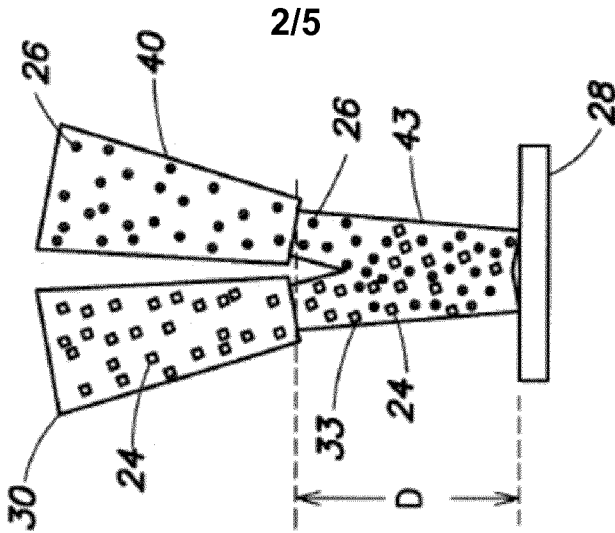


Figure 2c



3/5

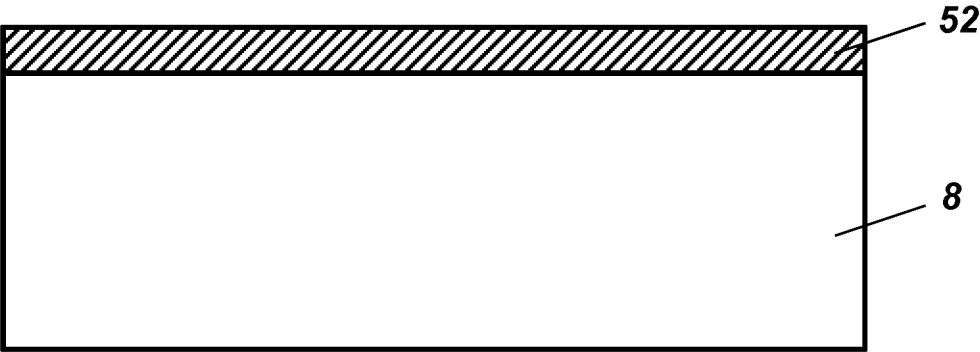


Figure 3

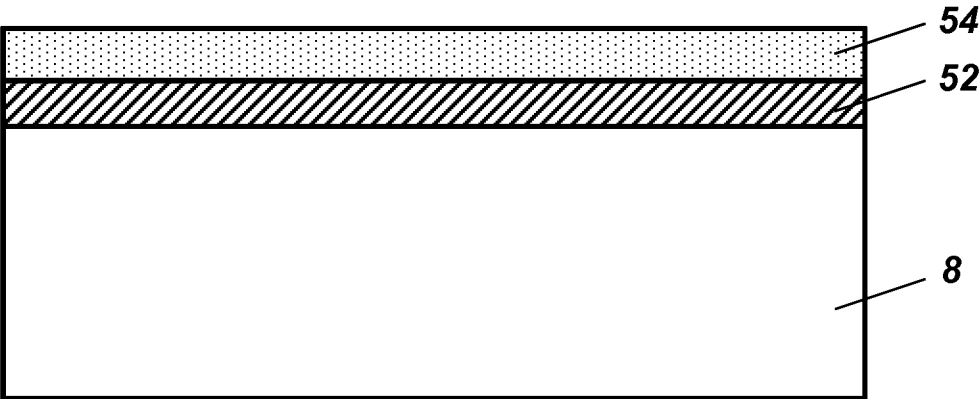


Figure 4

4/5



Figure 5

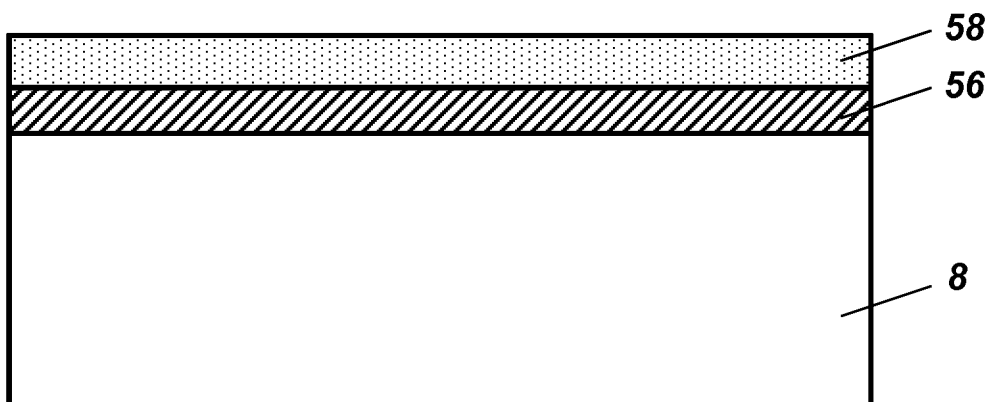
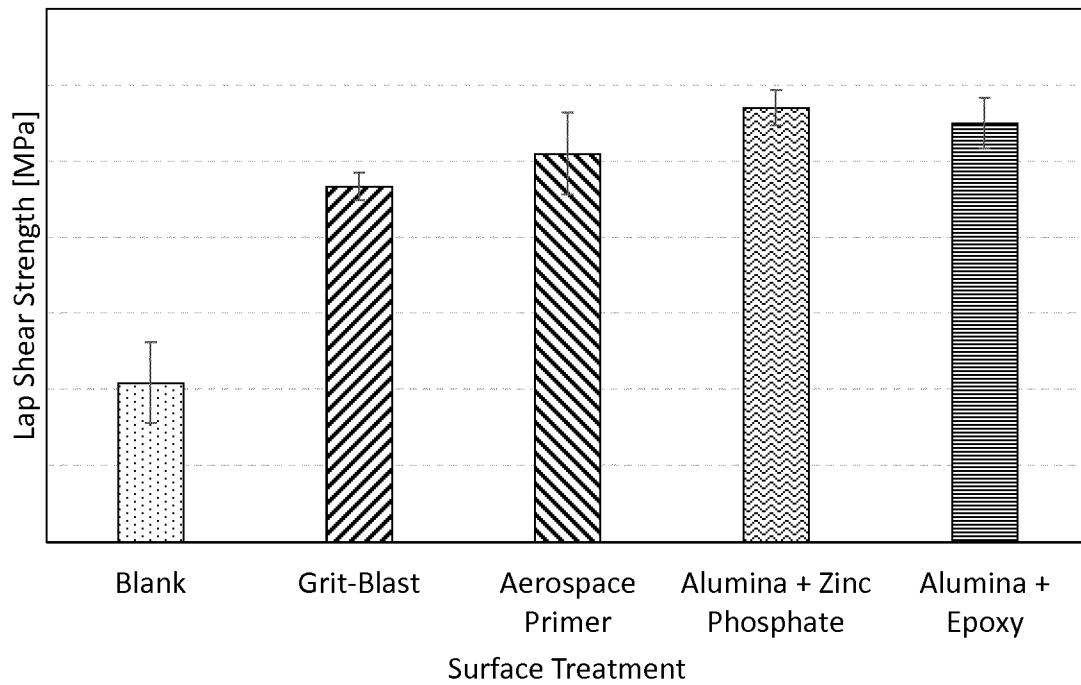


Figure 6

5/5

**Figure 7**

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/EP2015/055999

### Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

### Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-14, 42-53(completely); 32-41, 68-73(partially)

#### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2015/055999

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C23C24/04 B24C1/00 B24C3/02 B24C11/00  
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C B24C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, COMPENDEX

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 8 119 183 B2 (O'DONOGHUE JOHN GERARD [IE] ET AL) 21 February 2012 (2012-02-21) cited in the application	1-11, 32-34, 36-39, 41-50, 68-70, 72,73
A	claims 1, 3,5,30-32,61,72,85-87,91-93; figures 1,9; examples 1,8 column 8, line 37 - column 9, line 53 column 13, line 5 - line 12 column 14, line 16 - line 65 column 16, line 53 - line 66 ----- -/--	12-14, 40, 51-53,71



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

25 June 2015

Date of mailing of the international search report

02/09/2015

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2  
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Fax: (+31-70) 340-3016

Authorized officer

Ruiz Martinez, Maria

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2015/055999

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 069 418 A1 (AKZO NV [NL]) 12 January 1983 (1983-01-12)  page 1, line 3 - page 2, line 9; claims 1-12; example 1 page 5, line 5 - line 25 -----	1-3,11, 40-44, 50,70-73
X	US 2002/081243 A1 (HE TING [US]) 27 June 2002 (2002-06-27)  paragraphs [0023], [0028], [0030] - [0032], [0033]; claim 3; figure 2 -----	1-3,11, 14, 32-35, 53,70, 72,73
X	DE 10 2004 007361 A1 (INNOVENT EV [DE]) 9 September 2004 (2004-09-09)  paragraphs [0001], [0004] - [0007], [0013] - [0017]; claims 1-2 -----	1-3,7,8, 11-13, 41-44, 46,47, 50-52, 70,72,73

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2015/055999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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			US 2002081243 A1 27-06-2002
			WO 03009934 A1 06-02-2003
DE 102004007361	A1	09-09-2004	NONE

**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-14, 42-53(completely); 32-41, 68-73(partially)

Process for treating a substrate such as to form a corrosion inhibiting coating on the substrate and product thereof.

---

2. claims: 15-31, 54-67(completely); 32-41, 68-73(partially)

Process for treating a substrate such as to form an adhesion promotion coating on the substrate and product thereof.

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