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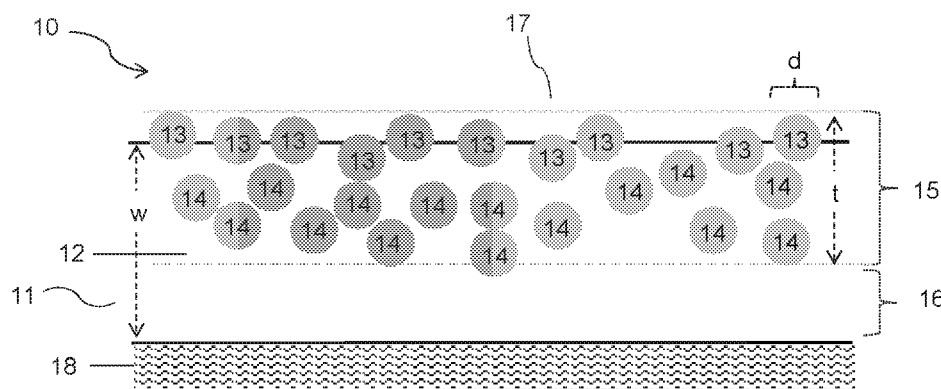


Figure 1

(57) Abstract: The invention provides an anti-fouling covering, comprising: a malleable film comprising at least a first layer of polymer; and particles having anti-fouling properties embedded in a retentive matrix of the polymer, the particles discontinuously arranged in an embedment layer which comprises: i) a surface population of the particles partially exposed on an anti-fouling surface of the anti-fouling covering; and ii) a submerged population of the particles submerged in the matrix beneath the surface population of the particles, wherein the anti-fouling covering inhibits fouling of a fouling-prone surface covered by the covering, the particles of the submerged population contributing to fouling inhibition by fluidly communicating with the anti-fouling surface.



Anti-fouling coverings and methods and apparatus for producing the same

Technical Field

[1] The present invention relates to anti-fouling coverings for protecting fouling-prone surfaces, to methods and apparatus for producing the anti-fouling coverings and to methods of protecting fouling-prone surfaces against fouling with the coverings. In particular, the anti-fouling coverings include a malleable film comprising at least a first layer of polymer, and particles having anti-fouling properties embedded in a retentive matrix of the polymer.

Background of Invention

[2] Implantation of particles into surfaces is an area of interest in a number of fields. For example, particle-functionalized surfaces may be provided with useful functional properties of the particles, such as anti-microbial or anti-fouling properties.

[3] In the context of the present invention, fouling refers to the deposition or accumulation of unwanted material on a solid surface, most often in an aquatic environment. Fouling can involve living organisms (referred to as "biofouling") or non-living substances that are inorganic or organic in nature. The solid surface is intended to perform some function and fouling can impede or interfere with that function. Fouling may also give rise to environmental or health issues. For these reasons, fouling is preferably reduced or avoided altogether.

[4] Biofouling of submerged surfaces tends to occur in all aqueous environments, but is particularly prevalent in marine environments. Marine biofouling has enormous economic and technical impacts on shipping, marine exploration, offshore oil and gas rigs, power and desalination plants and aquaculture. Historical approaches to mitigating biofouling have included the application of biocidal claddings or coatings to fouling-prone surfaces. Copper-containing paints are commonly used, although copper particles have also been incorporated into thermosetting adhesive compositions applied to marine surfaces, as described for example in US 5,284,682. Although such measures are routinely applied in the shipping industry, the need for regular re-coating presents an ongoing economic challenge, particularly as the coatings typically cannot be applied at sea. Furthermore, many types of maritime

equipment, such as instrumentation for conducting scientific measurements, are not amenable to the application of paints or similar coating compositions.

[5] Anti-fouling properties have also been imparted by spraying particles with anti-fouling properties onto fouling-prone surfaces. For example, as described in US 4,751,113, a continuous layer of metal or metal alloy is deposited by thermal spraying of a surface with high velocity molten or semi molten metal particles. While potentially useful for large-scale structures such as ship hulls, this method is not suited for many important marine applications, particularly those involving thermally sensitive surfaces or fragile equipment.

[6] An alternative approach, suitable for protecting polymeric surfaces against fouling, is described in WO2012/006687. Anti-fouling particles are sprayed onto the polymeric surface at a velocity sufficient to embed and elastically retain the particles in the solid polymer without the need for an adhesive. For example, polyethylene panels were cold-sprayed with copper or zinc particles and shown to then be resistant against biofouling. The embedded particles were either directly exposed at the polymer surface or in open fluid communication with the surface via shallow impact channels, thereby remaining available to contribute to fouling inhibition. This cold-spray surface functionalisation method is effective for protecting marine equipment which has suitable polymeric surfaces in which anti-fouling particles may be embedded.

[7] However, many examples of marine equipment susceptible to fouling do not have polymeric surfaces amenable to functionalisation with cold-sprayed particles. Furthermore, polymeric surfaces embedded with anti-fouling particles have a limited effective lifetime due to the eventual depletion of the active anti-fouling agent released by the particles. Although in some cases the anti-fouling properties may be replenished by re-spraying the surface, this is frequently not possible due to deterioration of the polymeric material, or is not conveniently achievable in the marine use environment. Moreover, limited loadings of anti-fouling particles were achieved with the methods of WO2012/006687, as continued cold-spraying of polymeric surfaces with anti-fouling particles was found to erode the polymeric surface rather than embedding additional particles once a threshold loading was exceeded.

[8] There is therefore an ongoing need for new methods to protect surfaces, particularly in the marine environment, against fouling. Preferably, such surfaces should be provided with long-lasting protection as a result of high loadings and/or prolonged release of active anti-fouling agents at the surface. Moreover, it is desirable that the anti-fouling surface protection should be renewable, and in particular that the replenishment of anti-fouling properties should be achievable in a marine environment where the fouling-prone surface is located and without the need for specialised application equipment.

[9] A reference herein to a patent document or other matter which is given as prior art is not to be taken as an admission that the document or matter was known or that the information it contains was part of the common general knowledge as at the priority date of any of the claims.

Summary of Invention

[10] The inventors have now developed a thin and malleable anti-fouling covering which may conveniently be applied to a variety of fouling-prone surfaces, including non-planar surfaces, non-polymeric surfaces and surfaces of sensitive equipment for which satisfactory anti-fouling mitigation has previously not been available. Advantageously, the anti-fouling covering may be applied in the marine use environment where the surface requiring protection is located. Furthermore, the anti-fouling protection of the surface may be conveniently renewed as required by simply removing a depleted covering and replacing it with a fresh anti-fouling covering.

[11] The anti-fouling cover of the invention comprises a thin, malleable, polymeric film which is embedded with particles having anti-fouling properties. The anti-fouling particles, including sub-surface embedded particles, contribute to fouling inhibition via fluid communication with the anti-fouling surface of the covering.

[12] The inventors have further developed methods and apparatus for producing the anti-fouling covers, by which the anti-fouling particles may be embedded into the malleable film with high mass loadings and thick embedment layers (relative to the film) without disintegrating the fragile film.

[13] As used herein, the term "anti-fouling" refers to a property whereby the build-up of inorganic and/or organic species on a surface is reduced or avoided altogether. Reducing or preventing the accumulation of such species on a surface may be advantageous for a variety of reasons, such as efficiency and/or hygiene/health. The species in question may be such things as biomatter or organic or inorganic compounds that manifest themselves as scale or corrosive deposits.

[14] The present invention is considered to have particular utility in reducing or preventing biofouling, which is the accumulation of unwanted biomatter on a surface as a result of the surface being exposed to some form of aqueous environment, including fresh water, salt water or water that has condensed on a surface. Examples of biofouling include the formation of biofilms and algae, and the accumulation and proliferation of microorganisms, such as the bacterium *Legionella* that is responsible for Legionnaires' disease. Biofouling may also be due to "macro-fouling" species, such as barnacles, mussels, seaweed and the like.

[15] In accordance with a first aspect the invention provides an anti-fouling covering, comprising: a malleable film comprising at least a first layer of polymer; and particles having anti-fouling properties embedded in a retentive matrix of the polymer, the particles discontinuously arranged in an embedment layer which comprises: i) a surface population of the particles partially exposed on an anti-fouling surface of the anti-fouling covering; and ii) a submerged population of the particles submerged in the matrix beneath the surface population of the particles, wherein the anti-fouling covering inhibits fouling of a fouling-prone surface covered by the covering, the particles of the submerged population contributing to fouling inhibition by fluidly communicating with the anti-fouling surface.

[16] In some embodiments, the malleable film has a thickness of less than 1 mm, preferably less than 0.75 mm, such as less than 0.5 mm. This may provide the necessary flexibility for the anti-fouling covering to closely conform to non-planar fouling-prone surfaces when applied, while not adding undue bulk to equipment covered by the anti-fouling covering. In some embodiments, the total thickness of the anti-fouling covering, including any additional polymeric or adhesive layers, is less than 1 mm, or less than 0.75 mm.

[17] In some embodiments, the particles have an average particle size of greater than 40 microns, preferably greater than 45 microns, more preferably greater than 50 microns. It has been found that larger particles result in both higher mass loadings and embedment depths in the anti-fouling coverings when produced by a spray method. In some embodiments, the total loading of particles in the embedment layer is greater than 300 g/m^2 , preferably greater than 400 g/m^2 , more preferably greater than 500 g/m^2 . However, the particles may have an average particle size of less than 200 microns, preferably less than 150 microns, more preferably less than 100 microns, to allow for their embedment in the thin malleable film.

[18] The embedded particles are arranged in an embedment layer. As used herein, an "embedment layer" is a layer of embedded particles, the layer being substantially in the plane of the malleable film and having an average thickness greater than the average particle size of its constituent embedded particles. In some embodiments, the embedment layer has an average thickness of at least twice the average particle size, preferably at least three times, or at least four times the average particle size. The embedment layer may thus have an average thickness of greater than 100 microns, or greater than 150 microns. It is considered that thicker embedment layers may in some embodiments provide not only greater loadings of anti-fouling particles, but also prolonged anti-fouling lifetimes due to delayed release of active anti-fouling agents from some of the particles.

[19] In some embodiments, the mass ratio (g/g) of the particles to the polymer in the first layer is above 0.3 : 1, such as above 0.5 : 1. Advantageously, a high loading of anti-fouling particles is thus provided in a very lightweight surface covering.

[20] In some embodiments, the anti-fouling covering further comprises a substantially particle-free sublayer of the first layer of polymer beneath the embedment layer. In other embodiments, the embedment layer extends from the anti-fouling surface through the entire thickness of the first layer of polymer. In some embodiments, the particles are distributed substantially homogeneously through the embedment layer in the thickness direction. The malleable film may further comprise a second polymeric layer adjacent to and beneath the first layer, the second polymeric layer having a Shore hardness greater than that of the polymer of the first layer. The second polymeric layer may be useful as a backstop to retain particles

within the first layer or to protect the integrity of the malleable layer when producing the film, for example when the polymer of the first layer is soft.

[21] The particles are retained in the matrix of the polymer without an extraneous adhesive or binder. Instead, the particles are elastically retained in the matrix of polymer. Suitable polymers may include thermoplastic or thermoset polymers, for example a thermoplastic polyurethane.

[22] The anti-fouling covering may further comprise impact channels formed during embedment of the particles, wherein the particles of the submerged population contribute to fouling inhibition by fluidly communicating with the anti-fouling surface via the impact channels. At least some of the impact channels may comprise a plurality of the particles, i.e. at least two, and in some embodiments, three or even more particles. The location of multiple particles in impact channels connected to the anti-fouling surface allows the formation of thicker embedment layers and/or higher particle loadings, while nevertheless permitting the particles to contribute to the anti-fouling action of the covering by fluid communication with the anti-fouling surface.

[23] The plurality of particles in the impact channels may in some cases comprise a particle from the submerged population located at the end of an impact channel and a particle from the surface population located in the throat of the impact channel. In these or other cases, the plurality of particles in an impact channel may comprise two or more particles from the submerged population. The plurality of particles in the impact channels may be adjacent and touching and/or they may be spaced apart.

[24] The particles of the surface population inhibit fouling of the anti-fouling surface due to their direct exposure on the surface. In some embodiments, at least some of the particles of the submerged population are in open communication with the anti-fouling surface, for example via impact channels, such that when exposed to the fouling environment, active anti-fouling agents released from the particles migrate to the surface, thereby contributing to anti-fouling inhibition. It is advantageous that the particles retain functionality when embedded beneath the exposed surface of the covering, since the particles are then protected from conditions (for example wave

action or currents) that may be physically erosive or result in overly rapid release of the active anti-fouling agent.

[25] In some of these or other embodiments, however, at least some of the particles of the submerged population are not in open communication with the anti-fouling surface of the covering, as a result of blocking by one or more particles located closer to the surface (typically located in the same impact channel). When the anti-fouling surface is first exposed to fouling conditions in use, for example by immersion in sea water, the blocked submerged particles will thus not initially contribute to inhibition of fouling. However, as the blocking particles release an active anti-fouling agent over an extended period of time, they hollow out, shrink, develop porosity and/or completely dissipate. In this manner, the initially blocked particles are eventually placed in fluid communication with the anti-fouling surface, and are thus enabled to contribute to fouling inhibition. Advantageously, this delayed action may extend the anti-fouling lifetime of the anti-fouling covering, particularly when higher particle loadings and/or relatively thicker embedment layers are used such that a greater proportion of the particles are initially blocked.

[26] The embedded particles are discontinuously arranged (i.e. they do not form a continuous layer) in the matrix of polymer. The particles may be present in the embedment layer as individually separated particles and/or as aggregates or clusters of optionally touching particles. However, they do not form a continuous surface or sub-surface layer. This has a number of advantages as follows:

- The effective life of the anti-fouling covering may be increased because the active particles are embedded in (including submerged within) a retentive polymeric matrix and are thus protected from attrition or erosion at the anti-fouling surface.
- The effective life of the anti-fouling covering may be increased by controlling the distribution, availability and position of the active particles.
- Continuous layers of anti-fouling materials can restrict the range of movement of the anti-fouling covering, thus preventing the application to non-planar surfaces; this issue is avoided using the present approach.

- The use of discontinuously embedded particles of suitably active material may be less expensive than providing a continuous layer due to the reduced volume of active material required to protect the same area of a fouling-prone surface.
- The particles are typically embedded in the malleable film by spraying, which inherently provides a discontinuous arrangement of embedded particles under conditions where the malleable film is not degraded by the sprayed particles.
- Combinations of particle and polymer may be selected without concern for normal continuous coating requirements with respect to particle/substrate adhesion and particle/particle cohesion.

[27] In some embodiments, the anti-fouling properties of the particles are provided by a chemical release mechanism. The particles may comprise a material selected from the group consisting of copper, zinc and compounds and alloys composed therefrom.

[28] The anti-fouling covering may further comprise an adhesive layer disposed on the malleable film for adhering to a fouling-prone surface. Alternatively, the malleable film may be thermoformable to adhere to a three-dimensionally structured fouling-prone surface. The anti-fouling covering may be disposed on a release layer, which may assist in the production of the covering and permit the covering to be provided as a roll without blocking.

[29] In accordance with another aspect the invention provides a method of producing an anti-fouling covering, the method comprising: a) resiliently retaining a malleable film comprising at least a first layer of polymer against a backing surface; and b) spraying a jet of particles having anti-fouling properties onto the first layer of polymer of the malleable film resiliently retained against the backing surface at a suitable impact velocity to embed the particles in a retentive matrix of the polymer, the particles thereby becoming discontinuously arranged in an embedment layer, wherein the resilient retention against the backing surface inhibits disintegration of the malleable film upon impact by the particles.

[30] In some embodiments, the embedment layer thus produced comprises: i) a surface population of the particles partially exposed on an anti-fouling surface of the

anti-fouling covering; and ii) a submerged population of the particles submerged in the matrix beneath the surface population of the particles.

[31] The method may further comprise tensioning the malleable film before spraying the jet of particles onto the first layer of polymer. It is considered that tensioning the film may in some embodiments cooperate with the resilient retention of the malleable film against the backing plate to further protect the film against disintegration when impacted with the sprayed particles.

[32] The malleable film may be resiliently retained against the backing surface by a compression assembly which comprises an aperture through which the jet of particles is sprayed onto the first layer of polymer. The width of the aperture is preferably less than four times the width of the jet, more preferably less than twice the width of the jet, and most preferably only as wide as needed to spray the jet of particles through it, such that the exposed area of film around the jet-impacted area of polymer is minimised.

[33] In some embodiments, the compression assembly comprises a front clamping plate configured to press the malleable film against the backing surface, and the aperture is a slot in the front clamping plate. In other embodiments, the compression assembly comprises rollers configured to press the malleable film against the backing surface, and the aperture is a slot between the rollers. In either case, spraying the jet of particles may comprise traversing the jet along the length of the slot so provide an even loading of embedded particles. The jet may be traversed over the malleable film at a speed of less than 1 m/s.

[34] The method may further comprise: c) feeding the malleable film over the backing surface to expose unsprayed portions of the first layer of polymer; and d) repeating steps a) and b). In this manner, a continuous web of anti-fouling covering, with substantially constant anti-fouling particle loadings along its length, may be produced. The malleable film may be fed by unspooling a web of the malleable film from an unwind roll.

[35] In some embodiments, the malleable film has a thickness of less than 1 mm, preferably less than 0.75 mm, such as less than 0.5 mm. The particles may have an average particle size of greater than 40 microns, preferably greater than 45

microns, more preferably greater than 50 microns. In some embodiments, the total loading of particles in the embedment layer after embedding the particles is greater than 300 g/m^2 , preferably greater than 400 g/m^2 , more preferably greater than 500 g/m^2 .

[36] The impact velocity for embedding the particles may be greater than 200 m/s, preferably greater than 300 m/s, and the jet of particles may optionally be heated to a temperature of between about 50°C and 300°C . The width of the jet impacting the malleable film is generally less than 20 mm, and may be less than about 10 mm.

[37] In accordance with another aspect, the invention provides an anti-fouling covering, produced by the method of any of the embodiments disclosed herein.

[38] In accordance with yet another aspect, the invention provides an apparatus for producing an anti-fouling covering, the apparatus comprising: a) a backing surface; b) a retaining arrangement configured to resiliently retain a malleable film comprising at least a first layer of polymer against the backing surface; and c) a spraying arrangement configured to spray a jet of particles having anti-fouling properties onto the first layer of polymer of the malleable film resiliently retained against the backing surface at a suitable impact velocity to embed the particles in a retentive matrix of the polymer. In use, the resilient retention against the backing surface inhibits disintegration of the malleable film upon impact by the particles.

[39] The apparatus may further comprise: d) a tensioning arrangement for tensioning the malleable film. The backing surface may be a planar sheet, or alternatively a rotating roller or drum. The retaining arrangement may comprise a compression assembly, the compression assembly comprising an aperture through which the jet of particles is sprayed onto the first layer of polymer. The width of the aperture is preferably less than four times the width of the jet, more preferably less than twice the width of the jet, and most preferably only as wide as needed to spray the jet of particles through it, such that the exposed area of film around the jet-impacted area of polymer is minimised.

[40] The compression assembly may comprise a front clamping plate configured to press the malleable film against the backing surface, the aperture being a slot in the front clamping plate. Alternatively, the compression assembly comprises

rollers configured to press the malleable film against the backing surface, and the aperture is a slot between the rollers. In either case, the apparatus may further comprise a traversing arrangement for traversing the jet of particles along the length of the slot. In some embodiments, the spraying arrangement comprises a cold spray machine.

[41] The apparatus may further comprise: e) a feeder for feeding the malleable film over the backing surface to expose unsprayed portions of the first layer of polymer.

[42] In accordance with another aspect, the invention provides a method of protecting a fouling-prone surface against fouling, the method comprising covering the fouling-prone surface with the anti-fouling covering of any of the embodiments disclosed herein.

[43] In some embodiments, covering the surface comprises adhering or thermoforming the anti-fouling covering to the fouling-prone surface, preferably adhering.

[44] Where the terms "comprise", "comprises" and "comprising" are used in the specification (including the claims) they are to be interpreted as specifying the stated features, integers, steps or components, but not precluding the presence of one or more other features, integers, steps or components, or group thereof.

[45] Further aspects of the invention appear below in the detailed description of the invention.

Brief Description of Drawings

[46] Embodiments of the invention will herein be illustrated by way of example only with reference to the accompanying drawings in which:

[47] Figure 1 is a schematic diagram of an anti-fouling covering comprising a malleable film including a first layer of polymer, and particles having anti-fouling properties embedded in a matrix of the polymer, according to an embodiment of the invention.

[48] Figure 2 is a schematic diagram depicting idealised embedment modes of the embedded particles of Figure 1.

[49] Figure 3 is a schematic diagram of an anti-fouling covering comprising a malleable film including a first layer of polymer and a second polymeric layer, and particles having anti-fouling properties embedded in a matrix of the polymer, according to another embodiment of the invention.

[50] Figure 4 is a schematic diagram of an anti-fouling covering on a release layer, the anti-fouling covering comprising a malleable film including a first layer of polymer, and particles having anti-fouling properties embedded in a matrix of the polymer, according to another embodiment of the invention.

[51] Figure 5 is a schematic diagram of an apparatus for producing an anti-fouling covering, according to an embodiment of the invention.

[52] Figure 6 is a schematic diagram of an apparatus for producing an anti-fouling covering, according to another embodiment of the invention.

[53] Figure 7 is a photograph of a malleable film (Film 1B) sprayed with a jet of particles and thus disintegrated, as prepared in Example 1.

[54] Figure 8 is a cross-sectional optical microscope image of an anti-fouling covering according to the invention (Film 1A), as produced in Example 1.

[55] Figure 9 is a photograph of an apparatus for producing an anti-fouling covering according to the invention, as used in Example 2.

[56] Figure 10 is a cross-sectional optical microscope image of an anti-fouling covering (with initial malleable film thickness of 0.31 mm) according to the invention (Film 2B), as produced in Example 2.

[57] Figure 11 is a cross-sectional optical microscope image of an anti-fouling covering (with initial malleable film thickness of 0.15 mm) according to the invention (Film 2C), as produced in Example 2.

[58] Figure 12 is a secondary electron SEM image of the anti-fouling surface of the anti-fouling covering (Film 2C) depicted in Figure 11.

[59] Figure 13 is a cross-sectional optical microscope image of a cold sprayed soft silicone film (Film 1C), as produced in Example 1.

[60] Figure 14 is a secondary electron SEM image of the surface of the cold-sprayed soft silicone film (Film 1C) depicted in Figure 13.

[61] Figure 15 is a photograph of an anti-fouling covering according to the invention (Film 1A), after exposure to marine biofouling conditions for 294 days (in Example 3).

[62] Figure 16 is a photograph of a covering (Film 1C) after exposure to marine biofouling conditions for 295 days (in Example 3).

Detailed Description

[63] The present invention relates to an anti-fouling covering suitable for protecting a fouling-prone surface against fouling. The covering includes a malleable film comprising at least a first layer of polymer; and particles having anti-fouling properties embedded in a retentive matrix of the polymer. The embedded particles are discontinuously arranged in an embedment layer which comprises: i) a surface population of the particles partially exposed on an anti-fouling surface of the anti-fouling covering; and ii) a submerged population of the particles submerged in the matrix beneath the surface population of the particles. When covering a surface exposed to fouling conditions, the anti-fouling covering inhibits fouling of the surface. The particles of the submerged population are able to contribute to the fouling inhibition by fluidly communicating with the anti-fouling surface.

[64] As will be described in greater detail hereafter, the present invention also relates to methods and apparatus for producing these anti-fouling coverings, and to methods of protecting a fouling-prone surface with the coverings.

Malleable film

[65] As used herein, a malleable film is a thin, flexible film which may be physically conformed to closely fit a non-planar surface without breaking or cracking. The anti-fouling covering of the invention is generally a thin, film-like covering that fits to the contours of a fouling-prone surface. The malleable film in which the anti-fouling particles are embedded is thus sufficiently flexible and resilient to be closely fitted to such surfaces, which may include non-planar regions such as corners, curved surfaces and the like. In order to provide the necessary flexibility, the malleable film typically has a thickness of less than 1 mm, such as less than 0.75 mm or less than 0.5 mm.

[66] The malleable film comprises at least a first layer of polymer, adjacent to and forming part of an exposed anti-fouling surface of the anti-fouling covering. The polymer of the first layer should therefore itself be sufficiently flexible to allow the malleable film as a whole to conform to a contoured surface.

[67] As will be described in greater detail hereafter, the anti-fouling coverings are generally produced by spraying a jet of particles onto the layer of polymer at an impact velocity sufficient to penetrate the polymer and become embedded in a retentive matrix of polymer. The mechanism of embedment involves deformation of the polymer and "trapping" of the particles. The kinetic energy of the particles is dissipated on collision with the polymer surface through deformation of the polymer, enabling at least a portion of the sprayed particles to penetrate the polymer surface. The polymer should have suitably elastic properties so that deformation of the polymer is partially recovered. This elastic "rebound" acts to reduce the diameter of the pathway through which the particle entered the layer to less than the diameter of the particle, thus resiliently retaining (i.e. mechanically adhering) the particle within the matrix of polymer. The elastic deformation is typically viscoplastic in nature, whereby deformation of the polymer caused by impact of the particles is only partially recovered, since it is important that the particles are not fully enclosed and thus may fluidly communicate with the surface of the covering when placed in anti-fouling service.

[68] In order to provide these properties, the polymer in which the particles are embedded may in some embodiments have an elastic modulus of no more than 3000 MPa, for example no more than 2500 MPa measured at room temperature. The elastic modulus may be no more than 2000 MPa, no more than 1500 MPa, no more than 1000 MPa or no more than 800 MPa. As used herein, elastic modulus is inclusive of Young's modulus and storage modulus, as measured according to ASTM D882.

[69] The hardness of the polymer in the first layer, as measured for example by the Shore Hardness D2 method with a Shore Durometer in accordance with ASTM D2240-05, is also expected to affect the embedment of particles. A Shore D2 hardness of less than 75, and more preferably less than 70, is preferred to allow formation of embedment layers with higher particle loadings (e.g. greater than 200 g/m², or greater than 300 g/m²).

[70] The polymer of the first layer may be a cured thermoset polymer or a thermoplastic polymer, and may be a homopolymer or a co-polymer. Here the term "cured thermoset polymer" means a polymer has been cured by a chemical reaction within the bulk of the polymer.

[71] Suitable polymers may include thermoplastic polyurethanes such as polyester, polyether and aliphatic polyurethanes, silicone elastomers, rubbers such as butyl, nitrile and natural rubbers, polyolefins such as polyethylene (for example low density and linear low density polyethylene), polyvinyl chloride (PVC) and poly(tetrafluoroethylene) (PTFE). In some embodiments, the polymer is a polyurethane.

[72] In some embodiments, the malleable film consists of only the first layer of polymer. In other embodiments, however, the malleable film further comprises a second polymeric layer adjacent to and beneath the first layer. The second polymeric layer, while still generally being flexible, may optionally be tougher or harder (for example, have a greater Shore hardness) than the first layer of polymer into which the particles are embedded, and is therefore more resistant to penetration by sprayed

particles. In some embodiments, the first layer of polymer is reinforced, for example by glass fibre woven fabric, mesh or the like.

Particles having anti-fouling properties

[73] The anti-fouling covering of the invention includes particles having anti-fouling properties, embedded in a polymeric layer of a malleable film. The particles may provide anti-fouling functionality to the anti-fouling surface of the covering by a chemical release mechanism. A chemical release mechanism for the purposes of the present invention includes any mechanism whereby an active anti-fouling agent is released by the particles, including decomposition of the particles, reaction of the particles with one or more reagents and/or release of one or more encapsulated chemicals from the particles.

[74] When the efficacy of the particles is due to a chemical release mechanism, the particles may be functionally effective without directly contacting species that are responsible for fouling. The particles thus retain functionality even when completely submerged in a matrix of the polymer, provided that they remain in fluid communication with the anti-fouling surface. When exposed to fouling conditions, for example in a marine environment, an active anti-fouling agent that is released from the submerged particles will gradually migrate to the anti-fouling surface of the covering. It is advantageous that the particles retain functionality when embedded beneath the exposed surface of the covering, since the particles are then protected from conditions (for example wave action or currents) that may be physically erosive or result in overly rapid release of the active chemical agent.

[75] The particles may be inorganic and/or organic particles, such as those disclosed in the art to possess anti-fouling properties. With respect to marine anti-fouling, particles of copper or compounds and alloys thereof (e.g. copper-nickel, copper-tin, copper-zinc or copper-aluminium alloys, cuprous oxide, cupric oxide), and particles of zinc or alloys and compounds thereof are preferred. Metallic copper and copper alloy particles may be particularly effective. Without wishing to be limited by any theory, it is considered that metallic copper particles release Cu^{2+} ions into seawater as the active anti-fouling agent. In one embodiment, bronze, a copper-tin alloy, is used as the chemical release of copper from this alloy is relatively low,

thereby extending the effective anti-fouling life of anti-fouling coverings including these particles.

[76] Other types of particle that may be used to prevent or reduce biofouling include particles of peptides, chitosan, silver, TiO₂ and ZnO. Other suitably active particles include photo-catalysts and chemicals (preferably organic chemicals) immobilized within a solid matrix which controls the release of the encapsulated anti-foulant. Optionally, a mixture of two or more different anti-fouling particles (for example particles with anti-biofouling action, e.g. copper or cuprous oxide, in combination with particles comprising e.g. copper pyrithione or zinc pyrithione) may be employed to provide anti-fouling coverings able to resist fouling by multiple mechanisms.

[77] As the anti-fouling covers of the invention are typically prepared by spraying anti-fouling particles onto a malleable film, the particles should generally be available in powder form. The particles should also be thermally and mechanically stable during the spray process.

[78] The particles should be of a suitable particle size for forming a discontinuous embedment layer in a malleable film of less than 1 mm thickness, and are thus generally smaller than 200 microns, and typically less than 100 microns. As the anti-fouling coverings of the invention are typically prepared by spraying anti-fouling particles onto the malleable film, the particle size should be in a range that allows the particles to be accelerated to high enough velocity to become embedded in the chosen polymeric film in an embedment layer including a population of submerged particles. Particles which are too small, such as below 1 micron, or below 10 microns, may not adequately penetrate the malleable film during spraying. Particles with larger sizes, such as those having average particle sizes above 20, or above 30, or above 40 microns, have higher momentum when sprayed at a given impact velocity, and are thus able to penetrate more deeply into a polymeric film. This may advantageously lead to the formation of higher particle loadings and thicker embedment layers. In some embodiments, therefore, the particles having anti-fouling properties may have an average particle size of between 20 and 200 microns, preferably between 30 and 100 microns, such as between 40 and 80 microns.

Average particle size may be measured by a number of common methods, such as laser diffractometry or sieve analysis. Unless otherwise indicated, average particle sizes disclosed herein are as measured with laser diffractometry, such as with a Malvern Mastersizer X instrument.

Anti-fouling surfaces of the coverings

[79] The covering includes a malleable film comprising at least a first layer of polymer; and particles having anti-fouling properties embedded in a retentive matrix of the polymer. A surface population of the particles is partially exposed on an anti-fouling surface of the anti-fouling covering, while a submerged population of the particles is submerged in the matrix beneath the surface population of the particles.

[80] The surface morphology of the anti-fouling surface is typically determined by the method of production, which generally involves spraying a jet of the particles onto the first layer of polymer of the malleable film, thereby embedding the particles (both surface and submerged populations) in a retentive matrix of the polymer. Impact of the particles on the polymer layer will create structural changes at the polymer surface due to deformation of the polymer. These structural changes are characteristic of the elastic (viscoplastic) deformation mechanism which enables the particles to be trapped within the polymer.

[81] In general terms, the particles of the surface population are embedded in craters or cavities that form in the polymer surface due to particle impact. Craters have raised edges extending above the original surface of the polymer formed by lateral and upward displacement of polymer as the particle impacts its surface. A cavity does not have such raised edges. Particles of the surface population may be located in craters and/or cavities, with a portion of the particles' surfaces extending above the polymer surface. If a particle becomes embedded in the polymer surface such that the portion of the particle with the largest dimension is beneath the polymer surface, the particle may be held in place as a result of the rim of the crater or cavity closing due to the inherent elasticity of the polymer. For spherical particles, the largest dimension will be the particle diameter.

[82] The surface of the anti-fouling covering may also comprise unfilled cavities and/or craters formed by impacts of particles that do not become embedded, or which become temporarily embedded but later detach from the surface as a result of further particle impacts or other forces on the surface.

[83] The surface of the anti-fouling covering generally also comprises impact channels formed by particles becoming embedded beneath the surface of the polymer as particles of the submerged population. The impact channels may comprise a plurality of particles, optionally including a surface-exposed particle in the throat of the impact channel. Multiple particles may become embedded in an impact channel via i) a first particle impacting the surface and becoming embedded below the surface of the polymer at the end of an impact channel, and ii) one or more further particles impacting the surface and becoming embedded in the same impact channel (which may be partially reconfigured as a result of the further impacts). Alternatively, i) a first particle impacting the surface becomes embedded in a crater or cavity on the polymer surface, and ii) a second particle impacts the first particle, thereby driving it sub-surface into the matrix of polymer, while itself (or subsequent particles) becoming embedded in the impact channel thus formed.

[84] The anti-fouling surface of the anti-fouling covering, generally comprising embedded particles, unfilled impact craters and impact channels as described, thus typically has a high degree of surface roughness, for example average surface roughness (Ra) as measured using a stylus profilometer or optical profiler. In some embodiments, the average surface roughness (Ra) may be greater than 1 microns, for example greater than 2 microns.

Anti-fouling coverings

[85] The anti-fouling covering of the invention is generally a thin, film-like covering capable of fitting closely to the profile of a fouling-prone surface. The covering thereby protects the surface against fouling, preferably without adding undue bulk or unacceptably compromising the functionality of the equipment or structure that includes the surface.

[86] An embodiment of the invention will now be described with reference to Figure 1, which is a schematic diagram of anti-fouling covering 10 comprising malleable film 11 and particles 13 and 14 having anti-fouling properties. Malleable film 11 comprises only a single layer of polymer 12, having a thickness (marked "w" in Figure 1) which is less than 1 mm to allow the necessary flexibility.

[87] Particles 13 and 14 are embedded in a retentive matrix of polymer 12 without an extraneous adhesive or binder, and are discontinuously arranged (i.e. they do not form a continuous layer) in embedment layer 15. Particles 13 and 14 may be present in embedment layer 15 as individually separated particles and/or as aggregates/clusters of particles. However, they do not form a continuous surface or sub-surface layer. Embedment layer 15 comprises both a surface population of particles 13, which are partially exposed at anti-fouling surface 17, and a submerged population of particles 14, which are submerged in the matrix of polymer 12 and are thus generally disposed beneath the surface population of particles 13.

[88] Anti-fouling covering 10 further comprises adhesive layer 18 disposed beneath malleable film 11, which is suitable for adhering anti-fouling covering 10 to a fouling-prone surface. Adhesive layer 18 may optionally be an acrylic, butyl, silicone or rubber adhesive layer, as known to those skilled in the art. Although not depicted in Figure 1, anti-fouling covering 10 may be disposed on a release layer, which allows the covering to be produced from and used as a roll without blocking.

[89] When applied to a fouling-prone surface, for example a surface of marine equipment, anti-fouling film 10 inhibits fouling since anti-fouling surface 17 is presented to the fouling environment instead of the underlying fouling-prone surface. Typically, anti-fouling particles 13 and 14 release an active anti-fouling agent over time by a chemical release mechanism. Surface particles 13 inhibit fouling of anti-fouling surface 17 due to their direct exposure to the fouling environment. Submerged particles 14 contribute to fouling inhibition by fluidly communicating with anti-fouling surface 17 when placed in fouling conditions, as will be further described hereafter.

[90] Particles 13 and 14 have a particle size marked "d" in Figure 1. Although Figure 1 depicts particles 13 and 14 with a uniform particle size "d", it will be appreciated that in practice a particle size distribution, having an average particle size "d", will be employed. In some embodiments, the average particle diameter is greater than 40 microns, such as between 40 and 80 microns. The thickness of embedment layer 15 (marked "t" in Figure 1) is generally at least twice the average particle size d, and preferably at least three times, or at least four times, the average particle size d. In the embodiment of Figure 1, however, the embedment layer does not extend through the entire thickness of the layer of polymer 12. Substantially particle-free sublayer 16 of polymer 12 is thus present beneath embedment layer 15.

[91] Anti-fouling covering 10 will now be further described with reference to Figure 2. Figure 2 depicts schematically the configuration of a number of partially exposed particles 13 (shown as particles 13a-13d in Figure 2) and submerged particles 14 (shown as particles 14a-14d in Figure 2) which are embedded in polymer 12. It will be appreciated that the arrangement of particles depicted in Figure 2 represents idealised embedment modes useful for understanding the principles of the invention, and that more complex three-dimensional arrangements of particles are in practice also likely to be obtained.

[92] Exposed surface particles 13a and 13b are elastically retained in cavities 22 formed in the surface 21 of polymer layer 12. Particle 13b is more deeply penetrated into the matrix of polymer 12 than particle 13a. Due to its shallow embedment, particle 13a may be susceptible to detachment from surface 21, leaving an unfilled impact cavity in surface 21.

[93] Submerged particles 14a and 14b are submerged within the matrix of polymer 12, being located beneath the level of polymer surface 21. Anti-fouling covering 10 comprises impact channels 23 which provide for fluid communication between particles 14a/14b and anti-fouling surface 17 when exposed to fouling conditions. Impact channels 23 may have a substantially narrower diameter than the particle size d, as a result of elastic rebound of polymer 12 after embedment of the particle. However, polymer 12 does not completely enclose submerged particles 14a and 14b after embedment, as particles sealed within the polymer matrix will no longer

be in fluid communication with surface 17, and therefore cannot contribute to fouling inhibition.

[94] Some impact channels, including impact channels 24 depicted in Figure 2, comprise two anti-fouling particles, such as surface-exposed particle 13d located in impact channel throat 25 and submerged particle 14d located at impact channel end 26. Particles located in the same impact channel may be spaced apart, as depicted for particles 13d and 14d. Alternatively, the particles may be adjacent and touching, as depicted for particles 13c and 14c. Although impact channels 24 depicted in Figure 2 comprise only two particles, including one surface-exposed and one submerged particle, it will be appreciated that impact channels may instead comprise three or more particles, of which none, one or even more than one may be partially exposed on anti-fouling surface 17.

[95] Submerged particles 14c or 14d may not be in direct communication with anti-fouling surface 17, as a result of the blocking of impact channel 24 by one or more shallower particles (such as particles 13c and 13d). Therefore, when anti-fouling surface 17 is first exposed to fouling conditions, for example by immersion in sea water, submerged particles 14c and/or 14d may not initially contribute to inhibition of fouling as particles 13c and 13d are able to do. However, as particles 13c and 13d release an active anti-fouling agent over an extended period of time, they will generally hollow out, shrink, develop porosity and/or completely dissipate. In this manner, particles 14c and 14d are eventually placed in fluid communication with anti-fouling surface 17, and are thus enabled to contribute to fouling inhibition. Advantageously, this delayed action may extend the anti-fouling lifetime of anti-fouling covering 10. Furthermore, increased loadings of submerged anti-fouling particles 14 and/or a thicker embedment layer 15, as made available by the invention, may increase both the amount of active anti-fouling agent available for release to anti-fouling surface 17 and extend the time-period of that release. This is due to the beneficial delay in establishing fluid communication between the most deeply penetrated submerged particles 14 and anti-fouling surface 17.

[96] Another embodiment of the invention will now be described with reference to Figure 3, which is a schematic diagram of anti-fouling covering 30 comprising

malleable film 31 and particles 33 and 34 having anti-fouling properties. Malleable film 31 comprises a first layer of polymer 32 (having a thickness marked " w_p " in Figure 3) and a second polymeric layer 36. Second polymeric layer 36, while still being flexible, has a greater Shore hardness than polymer 32. The total thickness of malleable film 31 (marked w_f in Figure 3) is typically less than 1 mm to allow the necessary flexibility. Although not depicted in Figure 3, anti-fouling covering 30 may optionally further comprise an adhesive layer and/or be on a release layer.

[97] Particles 33 and 34 are embedded in a retentive matrix of polymer 32, and are discontinuously arranged in embedment layer 35, which comprises a surface population of particles 33 partially exposed on anti-fouling surface 37 and a submerged population of particles 34. In the embodiment of Figure 3, the embedment layer extends from anti-fouling surface 37 through the entire thickness of the first layer of polymer 32. The thickness w_p of first layer of polymer 32 is sufficient to provide a desirable embedment layer thickness and particle loading. First layer 32 may therefore have a thickness w_p of at least twice the average particle size, and preferably at least three times, or at least four times, the average particle size of the embedded particles. Submerged particles 34 are generally not deeply embedded into second polymeric layer 36, although it is not excluded that some particles 34 may at least partially penetrate into layer 36 despite the greater Shore hardness.

[98] Another embodiment of the invention will now be described with reference to Figure 4, which is a schematic diagram of anti-fouling covering 40 comprising malleable film 41 and particles 43 and 44 having anti-fouling properties. Malleable film 41 comprises only a single layer of polymer 42 having a thickness (marked " w " in Figure 4) which is typically less than 1 mm to allow the necessary flexibility.

[99] Particles 43 and 44 are embedded in a retentive matrix of polymer 42, and are discontinuously arranged in embedment layer 45, which comprises a surface population of particles 43 partially exposed on anti-fouling surface 47 and a submerged population of particles 44. In the embodiment of Figure 4, the embedment layer extends from anti-fouling surface 47 through the entire thickness of the layer of polymer 42 and thus the malleable film 41. The thickness of first layer of polymer 42 is sufficient to provide a desirable embedment layer thickness and particle

loading. First layer 42 may therefore have a thickness w of at least twice the average particle size, and preferably at least three times, or at least four times, the average particle size of the embedded particles.

[100] Anti-fouling covering 40 is disposed on release layer 48. Release layer 48, though preferably sufficiently flexible to permit rolling of anti-fouling covering 40, is formed from a hard polymer (or other suitably hard material) which is not easily penetrated upon impact by particles 44, as will be further described hereafter.

Methods and apparatus for producing an anti-fouling covering

[101] The present invention also relates to a method of producing an anti-fouling covering as described herein. The method includes the steps of a) resiliently retaining a malleable film comprising at least a first layer of polymer against a backing surface; and b) spraying a jet of particles having anti-fouling properties onto the first layer of polymer of the malleable film resiliently retained against the backing surface at a suitable impact velocity to embed the particles in a retentive matrix of the polymer. The particles thereby become discontinuously arranged in an embedment layer which comprises: i) a surface population of the particles partially exposed on an anti-fouling surface of the anti-fouling covering; and ii) a submerged population of the particles submerged in the matrix beneath the surface population of the particles. The resilient retention of the malleable film against the backing surface during spraying inhibits disintegration of the malleable film upon impact by the particles.

[102] The present invention also relates to an apparatus for producing an anti-fouling covering according to the invention and for performing the method of the invention. The apparatus comprises a backing surface, a retaining arrangement configured to resiliently retain a malleable film comprising at least a first layer of polymer against the backing surface and a spraying arrangement configured to spray a jet of particles having anti-fouling properties onto the first layer of polymer at a suitable impact velocity to embed the particles in a retentive matrix of the polymer. In use, the resilient retention of the malleable film against the backing surface during spraying inhibits disintegration of the malleable film upon impact by the particles.

Particle spray technology

[103] The method of the invention includes the step of spraying a jet of particles having anti-fouling properties onto the first layer of polymer at a suitable impact velocity to embed the particles in a retentive matrix of the polymer.

[104] In general terms particles are embedded in the malleable film by a spray mechanism in which the particles are accelerated to a suitable velocity, and thus have suitably high kinetic energy, such that when they contact the polymer surface they penetrate the polymer surface. Generally, the polymer of the first layer is deformed as the particles penetrate into it. The polymer then recovers or "rebounds" thereby squeezing and/or enveloping the particle and so securing it in place. Depending upon the energy of the particles a lesser or greater degree of penetration may be achieved. This process control may be advantageous as it allows the anti-fouling properties of the malleable film, or regions thereof, to be tailored.

[105] A variety of spray technologies may be employed to this end. The particular technology used should be capable of accelerating the particles to a suitably high velocity to cause the particles to become embedded in the polymer surface. It will be appreciated that the required impact velocity may vary depending on the properties of the polymer. It is also important that the spray technology and/or the impact velocity of the particles used do not irreversibly and adversely affect the properties of the malleable film, for example by undue heating at high temperature.

[106] In an embodiment, the particles are sprayed using cold-gas dynamic spraying (cold spraying). Cold spraying involves feeding particles into a high pressure gas flow stream which is then passed through a converging/diverging nozzle (such as a de Laval nozzle) that causes the gas stream to be accelerated to supersonic velocities. The particles are then directed in a jet onto a substrate surface. The process is generally conducted so as to maintain relatively low temperatures at the polymeric surface, below the melting point of the substrate.

[107] Cold-gas dynamic spraying is carried out at suitable temperatures that will not result in undue softening of the particles. In this regard it should be noted that to penetrate the polymer on impact the particles must be sufficiently solid/hard.

Softening of the particles may impair their ability to penetrate the polymer surface when sprayed. The particles should also be functionally active following spraying and it is possible, depending upon the mechanism by which the particles provide an anti-fouling effect, that the spraying conditions may influence this. For example, the particles may lose functionality if spraying results in significant surface oxidation of the particles. The conditions for cold- gas dynamic spraying will therefore be selected accordingly based on the particles being sprayed. The effect of spraying on the polymer surface should also be taken into account.

[108] The two conventional uses of cold spray are (a) the build-up of a coating layer above the surface of the substrate where the coating layer thickness is at least several times the average particle diameter and (b) the massive build-up of a deposit, at least several millimetres thick, which can subsequently be used as a free-standing component. In order for build-up of the particle material to occur, the particles must impact the substrate surface at a velocity exceeding a certain critical velocity. The critical velocity is material specific.

[109] The current invention is a departure from these two conventional uses of cold spray, where the particles are accelerated towards the malleable film by a cold spray device such that when they contact the polymer surface of the first layer they penetrate the polymer surface by deformation of the polymer. Depending upon the energy of the particles a lesser or greater degree of penetration may be achieved.

[110] However, the particles need not be accelerated to above the critical velocity for particle/particle cohesion. If indeed a given set of spray conditions were to result in the build-up of material on the initial, embedded layers of particles, such that a continuous coating layer might form on the substrate surface, then this build-up should be avoided by reducing the number of particle impacts on any given area of substrate. This may be achieved, for example, by lowering the powder feed rate and increasing the relative traverse motion between the spray nozzle and the substrate. In this context, it may also be desirable to use spray conditions that allow particles to be embedded but that prohibit coating build-up (i.e. by avoiding exceeding the particle critical velocity).

[111] This process control may be advantageous as it allows the anti-fouling properties of the polymeric film, or regions of the film, to be tailored. The desired distribution density of particles in the film may vary depending upon, amongst other things, the propensity of, for example, marine organisms to otherwise attach to the polymer (the nature of the marine environment will be relevant here) and the extent/longevity of anti-fouling protection required. An adequate and optimum distribution density can be determined by computer modelling, experiment or trial and error.

[112] Typically, the velocity of the gas stream results in a particle velocity in the range of 200 to 1200 m/s, for example in the range 300 to 1100 m/s, 350 to 1000 m/s or 400 to 900 m/s. The optimal impact velocity may be dictated by the nature of the polymer layer and the desired particle loading and embedment layer thickness.

[113] Although cold spraying is currently the preferred method of spraying a jet of particles onto the layer of polymer, it is envisaged that in some embodiments, for example where very soft polymers are used, lower impact velocities may be suitable. In these embodiments, low pressure gas systems such as grit blasting equipment may be utilised.

Methods and apparatus

[114] Embodiments of the invention will now be described with reference to Figure 5, which is a schematic diagram of apparatus 50 for producing an anti-fouling covering according to the invention. Apparatus 50 comprises backing surface 51, in the form of a planar metallic sheet, and a compression assembly for resiliently retaining malleable film 53 against backing surface 51, in the form of front clamping plate 52 which is also a planar metallic sheet. A web of malleable film 53, comprising at least a first layer of polymer and typically (but not necessarily) disposed on a release layer, may be fed between backing surface 51 and front clamping plate 52. Malleable film 53 may be fed over backing surface 51 by unspooling the film from unwind roll 55 and onto rewind roll 56.

[115] Apparatus 50 comprises an actuator mechanism (not shown) for urging front clamping plate 52 against backing surface 51 so as to resiliently retain malleable

film 53 against backing surface 51 with a compressive force. Backing surface 50 and front clamping plate 50 have complementary profiles such that malleable film 53 is evenly pressed between the two metallic sheets. Although depicted in Figure 5 as planar sheets, it will be appreciated that backing surface 51 and front clamping plate 52 may have other profiles, including curved profiles. For example, backing surface 51 may be a rotating drum or roller.

[116] Front clamping plate 52 includes slot 54 which extends across the width of the web of malleable film 53, and through which the first layer of polymer is exposed when malleable film 53 is resiliently retained against backing surface 51. Slot 54 is preferably only as wide as needed to spray the jet of particles through it and onto the exposed layer of polymer beneath. An unnecessarily wide slot may render malleable film 53 more susceptible to disintegration when sprayed with the jet of particles.

[117] Apparatus 50 further comprises a spraying arrangement configured to spray a jet of particles having anti-fouling properties onto the layer of polymer at a suitable impact velocity to embed the particles in a retentive matrix of the polymer. As depicted in Figure 5, the spraying arrangement comprises cold spray machine 57 having a spray nozzle 58 positioned at a suitable stand-off distance to deliver a jet of particles through slot 54 and onto the polymer layer of malleable film 53. Cold spray machine 57 is configured to allow the traversal of nozzle 58 along the length of slot 54 at a predetermined speed, typically below 1m/s, such that malleable film 53 may be sprayed across its width with a consistent loading of particles.

[118] Apparatus 50 optionally further comprises a feeder for feeding malleable film 53 over backing surface 51, in the form of grip plates 59. The web of malleable film 53 may be gripped between plates 59 and fed forward an appropriate increment over backing surface 51 by moving plates 59 in the direction depicted by the arrow marked "f" in Figure 5. Once the web is repositioned, grip plates 59 may be released and returned to their original position.

[119] With continued reference to Figure 5, a method of producing an anti-fouling covering with apparatus 50 will now be described. Malleable film 53, comprising at least a first layer of polymer, is unspooled from unwind roll 55, fed first between

backing surface 51 and front clamping plate 52 (with the first layer of polymer adjacent front clamping plate 52, and the release layer adjacent backing surface 51), then between grip plates 59, and re-spoiled onto rewind roll 56.

[120] Malleable film 53 is then resiliently retained against backing surface 51 by pressing front clamping plate 52 against backing surface 51. A jet of particles having anti-fouling properties is sprayed through slot 54 onto the exposed layer of polymer using cold spray machine 57, while traversing the jet of particles emitted from nozzle 58 along the length of slot 54. The resilient retention of malleable film 53 against backing surface 51, as a result of the evenly applied clamping force and particularly the narrow slot width, has been found to inhibit disintegration of the fragile film caused by warping and subsequent tearing. As a result, thin films with high particle mass loadings and thick embedment layers relative to the film thickness have been successfully produced.

[121] A number of additional process variables may affect the method reliability, and the loading and configuration of particles embedded in malleable film 53. Lower traversal speeds of the jet of particles will tend to produce a higher loading of particles in the layer of polymer. Generally, the jet of particles is thus traversed at a speed of less than 1 m/s. Optionally, multiple passes of the jet of particles may also be made over the same strip of polymer to increase the loading. However, it will be appreciated that too slow a traversal speed (or too many passes) may increase the risk of degradation or disintegration of malleable film 53 caused by mechanical or thermal stress.

[122] Higher impact velocities increase the momentum of the sprayed particles, and thus their average penetration depth into the polymer layer of malleable film 53. Impact velocities of particles sprayed with cold spray machines may be adjusted by methods available to those skilled in the art. For example, the gas pressure and/or pre-heat temperature of the accelerating gas jet may be routinely optimised. Higher gas pre-heat temperature may also increase the temperature of the jet of particles impacting the polymer layer. It is currently considered that higher jet temperatures may in some cases beneficially soften (without melting or degrading) the polymer during particle embedment, thereby permitting the formation of a thicker embedment

layer. Alternatively, the polymer may be heated by other means to achieve this benefit, for example via the backing surface.

[123] Inherently softer polymers in malleable film 53 will also generally permit greater penetration by cold sprayed particles, resulting in higher loadings and a thicker embedment layer. However, the polymer should be sufficiently resilient and elastically deformable to prevent excessive penetration and complete enclosure of particles in a sealing matrix of polymer, as this will preclude fluid communication with the anti-fouling surface of the anti-fouling cover.

[124] Larger particle sizes also increase the momentum of the sprayed particles, and thus their penetration depth into the polymer. Using the method of the invention, which protects fragile films during cold spray, it has been found possible to successfully embed copper particles with an average particle size of above 40 microns into thin polymeric films, thereby achieving loadings in excess of 500 g/m² and embedment layer thicknesses of up to 200 microns.

[125] The skilled person with the benefit of this disclosure will be able to select suitable materials and spray conditions for a specific application, including jet traversal speed, cold spray conditions (such as gas pressure and pre-heat temperature), polymer properties and particle sizes, with no more than routine experimentation.

[126] Once the exposed layer of polymer underneath slot 54 has been suitably sprayed with a jet of particles, malleable film 53 is released by unclamping front clamping plate 52 from backing surface 51. The web may then be fed forward over backing surface 51, optionally using grip plates 59, to expose an adjacent strip of unsprayed polymer beneath slot 54.

[127] By repeated sequential steps of i) feeding malleable film 53 over backing surface 51, ii) resiliently retaining malleable film 53 against backing surface 51, iii) spraying a jet of particles onto the polymer layer of malleable film 53, and iv) releasing malleable film 53, a continuous web of anti-fouling covering, with substantially constant anti-fouling particle loadings along its length, may be produced.

[128] With reference now to both Figure 5 and Figure 1, a method of producing anti-fouling cover 10 with apparatus 50 will be described. A web of malleable film 11, comprising first layer of polymer 12, adhesive layer 18 and optionally on a release layer is fed into apparatus 50 as described herein. Although not required, it is contemplated that malleable film 11 may further comprise a very thin (for example, micron scale) surface finish layer on top of polymer layer 12, which is broken up during the subsequent embedment of the particles. Such a layer may advantageously modulate the hardness of the polymeric layer upon initial impact with the particles, or may provide secondary functionalities such as UV resistance.

[129] A jet of particles 13 and 14 having anti-fouling properties is then sprayed onto layer of polymer 12 using cold spray machine 57, as described herein. The particles are sprayed at a suitable impact velocity to become embedded in polymer 12, thereby forming embedment layer 15. The mass loading of particles 13 and 14, and the thickness t of embedment layer 15, may be controlled by appropriate selection of polymer 12, the average particle size, the particle impact velocity, the traversal speed and the temperature of the jet, as described herein.

[130] With reference now to both Figure 5 and Figure 3, a method of producing anti-fouling cover 30 with apparatus 50 will be described. A web of malleable film 31, comprising at least first layer of polymer 32 and second polymeric layer 36, is fed into apparatus 50 as described herein.

[131] A jet of particles 33 and 34 having anti-fouling properties is then sprayed onto first layer of polymer 32 using cold spray machine 57, as described herein. The particles are sprayed at an impact velocity sufficient for at least a substantial fraction of particles 34 to penetrate through first layer of polymer 32 and impact the surface of polymeric layer 36. However, because of the greater Shore hardness of second polymeric layer 36, particles 34 are unable to deeply penetrate into polymeric layer 36. Initially sprayed particles 34 thus accumulate at the interface between first layer 32 and second polymeric layer 36, with subsequently impacting particles 34 and 33 being restricted to progressively shallower penetration depths until a surface population of particles 33 is embedded on anti-fouling surface 37. The thickness of embedment layer 35 thus created is primarily determined by the thickness of first

layer of polymer 32. This method may advantageously permit a homogeneous embedment distribution and/or a dense volumetric loading of particles in embedment layer 35 to be produced, in some cases without a necessity for rigorous control of the particle impact velocity.

[132] With reference now to both Figure 5 and Figure 4, a method of producing anti-fouling cover 40 with apparatus 50 will be described. A web of malleable film 41 comprising first layer of polymer 42, on release layer 48, is fed into apparatus 50 as described herein.

[133] A jet of particles 43 and 44 having anti-fouling properties is then sprayed onto first layer of polymer 42 using cold spray machine 57, as described herein. The particles are sprayed at an impact velocity sufficient for at least a substantial fraction of particles 44 to penetrate through first layer of polymer 42 and impact the surface of release layer 48. Because of its hardness, particles 44 are unable to penetrate release layer 48. Initially sprayed particles 44 are thus embedded in polymer 42 adjacent to release layer 48, with subsequently impacting particles 44 and 43 being restricted to progressively shallower penetration depths until a surface population of particles 43 is embedded on anti-fouling surface 47. Embedment layer 45 thus created extends through the entire thickness of malleable film 41. This method may advantageously permit very high loadings of anti-fouling particles to be embedded throughout the thickness of very thin anti-fouling coverings.

[134] Apparatus 50 depicted in Figure 5 may be used for semi-continuous production of anti-fouling coverings using the sequential feed-clamp-spray-release methodology described herein. However, the principles of the invention also extend to fully continuous processes for producing anti-fouling coverings.

[135] Depicted in Figure 6 is a schematic diagram of apparatus 60 for producing an anti-fouling covering according to another embodiment of the invention. Apparatus 60 comprises backing surface 61 in the form of the curved metallic surface of rotating drum 69. A web of malleable film 63, comprising at least a first layer of polymer and typically (but not necessarily) disposed on a release layer, may be fed over drum 69 by unspooling the film from unwind roll 65 and onto rewind roll 66.

[136] Apparatus 60 comprises a retaining arrangement configured to resiliently retain film 63 against backing surface 61 in the form of compression assembly 62, which includes rollers 62a and 62b. Rollers 62a and 62b are configured to apply a constant compressive force against drum 69 while rotating to permit constant forward feed of malleable film 63. Optionally, rollers 62a and 62b may be independently controlled (for example with master and slave control) to tension malleable film 53 in the web length direction over backing surface 63. The web may alternatively be tensioned over backing surface 63 via control of unwind roll 65 and rewind roll 66, or with separate tensioning rollers (not shown).

[137] Compression assembly 62 includes slot 64 between rollers 62a and 62b which extends across the width of the web of malleable film 63, and through which the first layer of polymer is exposed when malleable film 63 is resiliently retained against backing surface 61. Slot 64 is preferably only as wide as needed to spray the jet of particles through it and onto the exposed layer of polymer beneath. An unnecessarily wide slot may render malleable film 63 more susceptible to disintegration when sprayed with the jet of particles.

[138] Apparatus 60 further comprises a spraying arrangement configured to spray a jet of particles having anti-fouling properties onto the layer of polymer at a suitable impact velocity to embed the particles in a retentive matrix of the polymer. As depicted in Figure 6, the spraying arrangement comprises cold spray machine 67 having a spray nozzle 68 positioned at a suitable stand-off distance to deliver a jet of particles through slot 64 and onto the polymer layer of malleable film 63. Cold spray machine 68 is configured to allow the continuous or semi-continuous traversal of nozzle 68 along the length of slot 64 at a predetermined speed, such that malleable film 63 may be sprayed across its width. It will be appreciated that the traversal speed of nozzle 68 and the forward feed speed of the web over drum 69 must be suitably matched to ensure a sufficiently consistent loading of particles over the surface of malleable film 63. Alternatively, an array of nozzles 68 may be statically positioned along the length of slot 64 to deliver a series of adjacent particle jets onto the polymer layer of malleable film 63.

In use, malleable film 63 is continuously fed over rotating drum 69 from unwind roll 65 to rewind roll 66, while resiliently retaining and optionally also tensioning malleable film 63 against backing surface 61 with rollers 62a and 62b. A jet of particles is sprayed onto the layer of polymer exposed beneath slot 64, using cold spray machine 67. The resilient retention of malleable film 63 against backing surface 61, as a result of the compressive force and close spacing of rollers 62a and 62b, will inhibit disintegration of the fragile film during particle embedment. It is considered that tensioning of the film may cooperate with the compressive force of rollers 62a and 62b to further protect the film against disintegration when impacted with the sprayed particles.

Methods of protecting a fouling-prone surface against fouling

[139] The present invention also relates to a method of protecting a fouling-prone surface against fouling. The method comprises covering the fouling-prone surface with the anti-fouling coverings of the invention.

[140] The fouling-prone surface may be covered with the anti-fouling covering by any suitable method, including by adhering or thermoforming the anti-fouling covering to the profile of the surface. In some embodiments, the anti-fouling covering includes an adhesive layer for adhering the covering to a surface. In other embodiments, the anti-fouling covering may be adhered to the surface without an adhesive layer. For example, the malleable film may comprise a self-fusing polymer which adheres to itself when wrapped in overlapping layers over an object. The anti-fouling covering may be thermoformed to the substrate by any suitable thermoforming methods, including vacuum forming and heat shrinking, for example heat shrinking of tubular coverings onto the surface of an enclosed object. Other suitable methods of covering the surface may include cold-shrinking a tubular covering on an object or elastically retaining a stretchable covering on an object. In any of these embodiments, if the anti-fouling covering is provided on a release layer, the release layer should be peeled off before or during application of the anti-fouling covering to the fouling-prone surface.

[141] In some embodiments, the anti-fouling covering may be provided as an elongated tape on a roll. The tape may then be unwound from the roll,

simultaneously removing the release layer if present, and applied to the fouling prone surface. The tape may be wrapped around an object, with the layers partly or wholly overlapping. In other embodiments, the anti-fouling covering is supplied as a flexible sheet, which may be cut to size as needed for fitting to the fouling-prone surface.

[142] Suitable fouling-prone surface which may usefully be covered by the anti-fouling covering include (but are not limited to): ship hulls; pleasure craft hulls; speed sensors; oceanographic moorings; sensors such as dissolved oxygen (DO) probes, pH probes, current temperature depth (CTD) sondes, acoustic Doppler current profilers (ADCPs); buoys; cables; underwater camera bodies; underwater light bodies, seismic streamer cables and ancillary equipment; underwater autonomous vehicles such as ocean gliders and wave gliders; aquaculture equipment, finfish cages, feeding lines, aeration equipment including paddlewheel aerators, acoustic feeding sensors, current sensors; acoustic release apparatus for moorings, acoustic release buoys; relative navigation sensors; multibeam and other depth sensors; acoustic modems; subsea oil and gas equipment, buoyancy modules, flexible risers; wave and tidal energy componentry; fish telemetry sensors, and wildlife tags.

EXAMPLES

[143] The present invention is described with reference to the following examples. It is to be understood that the examples are illustrative of and not limiting to the invention described herein.

Materials

[144] A number of polymeric films were obtained for cold-spray functionalisation. Adhesive films comprising a thermoplastic polyurethane layer (with a very thin clear-coat surface finish) and an acrylic adhesive layer, on a release layer, were obtained from 3M and XPEL companies. These commercially available films included 3M Scotchgard™ Paint Protection Film SGH12 (0.31 mm polyurethane layer with micron-scale clear-coat, 0.05 mm adhesive), 3M Scotchgard™ Paint Protection Film SGH6 (0.15 mm polyurethane layer with micron-scale clear-coat, 0.05 mm adhesive), and XPEL Ultimate Paint Protection film (0.15 mm polyurethane layer with 13 micron clear-coat, 0.04 mm adhesive). Rolls of 300 mm width were used in the experiments.

[145] A single layer thermoplastic ether polyurethane film (0.48 mm, without adhesive or clear-coat) was cut into a strip with a width of 300 mm.

[146] A glass-cloth reinforced silicone rubber film (c.a. 0.33-0.41 mm silicone layer, 0.25-0.30 mm fabric layer, 0.09-0.15 mm adhesive) was obtained in the form of a roll of 300 mm width.

[147] Air atomised copper particles (average particles sizes of 40, 47, 58 and 84 microns) were used. Particle size distributions were measured using a Malvern Mastersizer X.

Example 1

[148] An apparatus was constructed for cold-spraying a malleable film as depicted in Figure 7. The apparatus included a planar backing plate (701) and a planar mask (702) with apertures (703) in it. Masks with apertures of different sizes and shapes were made; circular apertures with diameters from 50 to 155 mm, 50 × 50mm square apertures and rectangular apertures up to 155 × 230mm were employed. A CGT Kinetiks 4000 or a Plasma Giken PCS-1000 cold spray machine (704) was positioned to project a jet of particles (approximately 7 – 10 mm jet diameter) towards the mask plate, and moved by an ABB 6-axis robot in a raster pattern to cover the whole mask surface and exposed film.

[149] Virgin samples of SGH12 film were placed between the backing plate and the mask to expose the layer of polymer through the apertures. A jet of copper particles was then sprayed through the apertures and onto the layer of polymer using the cold spray machine.

[150] The experiments demonstrated that the malleable film was susceptible to disintegration via tearing when cold-sprayed with copper particles. Film 1B was sprayed with copper particles (average particle size 47 microns) using a 75mm diameter circular mask, and gas preheat conditions of 200 °C and 2.0 MPa and a nozzle traverse speed of 0.5 m/s. The SGH12 samples regularly tore under under these conditions, as depicted in Figure 7 (film 1B). It was discovered that the integrity of the film during cold spray embedment could be protected by i) application of a firm and consistent clamping force to press the film between the backing plate and the

mask; ii) reducing the size of the circular or rectangular aperture (e.g. from 155 mm to 50 mm); and iii) maintaining low intensity cold spray conditions (e.g. lower copper particle sizes and higher traverse speeds).

[151] As shown in Table 1 below (film 1A), SGH12 film was successfully cold sprayed with copper particles (average diameter 40 microns) to achieve a loading of 220 g/m^2 (determined by weighing the film before and after cold spraying) by using a square $50 \times 50 \text{ mm}$ mask, and gas preheat conditions of 150°C and 2.0 MPa and a nozzle traverse speed of 0.5 m/s .

[152] Depicted in Figure 8 is a cross-sectional optical microscope image of film 1A, showing the copper functionalised SGH12 film at the intersection between an unsprayed (i.e. masked) and a sprayed section. The SGH12 film comprises polyurethane layer 810, acrylic adhesive layer 811 and clear-coat surface finish 812. In the cold-sprayed section, embedment layer 813 is visible, composed of a discontinuous array of copper particles embedded in the polyurethane matrix, including both a surface population of copper particles 814 and a submerged population of copper particles 815. Embedment layer 813 is of variable thickness, but is approximately 100 microns thick on average. A particle-free sublayer 815 of polyurethane layer 810 is present beneath embedment layer 813.

[153] A glass-cloth reinforced silicone rubber film was cold-sprayed through a circular aperture (50 mm diameter) with copper particles (average particle size 84 microns) using 200°C gas pre-heat temperature without disintegrating the film (film 1C). A very high loading of 800 g/m^2 copper was thereby achieved (Table 1).

[154] Depicted in Figures 13 and 14 are a cross-sectional optical microscope image and a SEM image of the surface of film 1C. It can be seen from Figure 13 that the copper particles have penetrated deep into the silicone polymer layer, and in some cases have passed into the underlying reinforcing fabric layer. From Figure 14, it is evident that particles are almost entirely absent from the surface of the film. As a result of the softness of the silicone rubber polymer, the impact velocity of the particles sprayed onto the surface was too high to produce an embedment layer comprising both a surface population and a submerged population of particles.

Example 2

[155] Another apparatus was constructed for cold-spraying a malleable film as depicted in Figure 9. The apparatus included a planar metal backing plate (901) and a planar metal clamping plate (902) with a slot (903) of 10 mm width and 280 mm length in it. A Plasma Giken PCS-1000 cold spray machine (not shown in Figure 9) was held by an ABB 6-axis robot and moved left-to-right and back in long, horizontal passes. In each spray pass the jet of particles (approximately 7 - 10 mm jet diameter) was projected through and along the length of the slot.

[156] For each cold spray functionalisation experiment, a malleable film (904) comprising at least one layer of polymer was unspooled from a roll and fed as a web (width of 300 mm) between the backing plate and the front clamping plate to expose the layer of polymer through the slot, which extended perpendicularly across the width of the web. The front clamping plate was then clamped against the backing plate to compress, and thus resiliently retain, the film against the backing plate, using a pneumatic actuator (905).

[157] A jet of copper particles was then sprayed through the slot and onto the layer of polymer using the cold spray machine. The spray nozzle was traversed along the slot at a constant predetermined speed to spray the entire strip of polymer exposed beneath the slot. The cold-spraying conditions were controlled by selecting the copper particle size, the gas pressure and pre-heating temperature (and thus the velocity and temperature of the jet of particles) and the traverse speed.

[158] The web of film was then released by unclamping the front clamping plate, and the web was fed over the backing plate to expose an adjacent strip of unsprayed polymer beneath the slot. The film was again resiliently clamped between the backing plate and the front clamping plate, and the virgin polymer surface exposed beneath the slot was sprayed with the traversing jet of copper particles. By repeated sequential steps of feeding-clamping-spraying-unclamping, a web of malleable film (width of 300mm, length of up to 36m) was sprayed with a continuous loading of embedded copper particles (906). The clamping / unclamping and film feeding procedure was automated and timed in coordination with the robot movement by the

robot controller computer, which supplied digital 24 V signals to solenoid valves to move the actuators.

[159] A series of particle functionalised films (films 2A-2E), prepared with different malleable polymer films, copper particle sizes and cold spray conditions, was prepared as show in Table 1 (pressure 2.0 MPa; traverse speed 500 mm/s) using the apparatus depicted in Figure 9.

Table 1 Preparation of cold sprayed films (Experiments 1 and 2)

Film No.	Cold spray system	Polymeric film	Mask size	Gas pre-heat temperature (°C)	Copper particles size (micron)	Copper loading
1A	CGT	SGH12	50 × 50 mm	150	40	220
1B	Plasma Giken	SGH12	75 mm diameter	200	47	Tore
1C	CGT	Reinforced silicone	50 mm diameter	100	84	800
2A	Plasma Giken	SGH12	N/A	150	58	306
2B	Plasma Giken	SGH12	N/A	200	58	586
2C	Plasma Giken	SGH6	N/A	200	47	359
2D	Plasma Giken	XPEL Ultimate	N/A	200	47	247
2E	Plasma Giken	Ether Polyurethane	N/A	200	47	563

[160] Using the apparatus with the slotted clamping plate, a higher loading of copper particles (above 300 g/m²) could be achieved by increasing the average copper particle size to 58 microns, without tearing the SGH12 film (film 2A; c.f. film 1A).

[161] Even higher loadings (586 g/m²) could be achieved without disintegrating the film by increasing the gas pre-heat temperature of the cold spray machine from 150°C to 200°C (Film 2B). It is considered that the increased pre-heat temperature resulted in increased impact velocities of the particles on the polymer layer, and that

the increased temperature of the jet of particles may have also softened (but not melted or degraded) the film to allow deeper embedment.

[162] Depicted in Figure 10 is a cross-sectional optical microscope image of film 2B. The embedment layer is approximately 200 microns thick on average, as a result of the greater penetration depth of the particles into the polyurethane layer. A particle-free sublayer is present beneath the embedment layer.

[163] The thinner SGH6 film (0.15 mm polyurethane layer vs 0.31 mm for SGH12) was also successfully cold-sprayed with copper particles (average copper particle size 47 microns) using the 200°C gas pre-heat temperature, thus achieving a loading of 359 g/m² (film 2C). As depicted in the cross-sectional optical microscope image of Figure 11, the embedment layer of film 2C is of approximately 150-200 microns in thickness. The embedment layer extends most of the way through the layer of polyurethane polymer, the thickness of which has been substantially increased as a result of the copper particle loading. Multiple submerged particles are present within approximately 80 microns of the lower surface of the polyurethane layer, with one particle located approximately 30 microns from the lower surface.

[164] Depicted in Figure 12 is a secondary electron SEM image of the cold-sprayed surface of film 2C. The surface population of particles embedded discontinuously in the matrix of polymer is visible in the SEM image, with the surface having a coverage of approximately 29% copper, as calculated by image analysis software. In places, for example within circle 1201 marked in Figure 12, particles fully submerged in impact channels within the matrix of polymer can be observed.

[165] The XPEL Ultimate film was successfully cold sprayed with copper particles (average particle size 47 microns) using the 200°C gas pre-heat temperature, thus achieving a loading of 247 g/m² (film 2D). The lower loading compared with the SGH6 polymer (c.f. film 2C) is possibly due to different polymer hardness / impact properties in this product.

[166] Single layer ether polyurethane film was also successfully cold sprayed with copper particles (average particle size 47 microns) using the 200°C gas pre-heat temperature, thus achieving a loading of 563 g/m² (film 2E). Ether polyurethanes have superior hydrolysis resistance and UV stability compared with ester

polyurethanes, and may thus be particularly suitable for marine applications. The higher loading compared with the commercial adhesive tapes may be due to different polyurethane properties and/or the absence of the micron-scale clear-coat surface finish.

Example 3

[167] Films 1A and 1C, as prepared in Example 1, were evaluated in field trials. Film 1A comprised a sprayed area of 50 × 50 mm and Film 1C comprised a 50 mm diameter circle. Both films were adhered to a 6 mm thick grey industrial PVC panel to form a test board, which was suspended vertically in the ocean at the Queenscliff Cruising Yacht Club jetty on Sand Island, Queenscliff, Victoria Australia, at a depth of approximately 200 mm below the low tide mark. In this location, there is considerable tidal flow perpendicular to the face of the panels.

[168] The test board was raised approximately monthly for inspection of the films. To remove silt and other loosely adhered material, each sample was given a light water jet with fresh water of no more than 2 N force (measured using an electronic scale; 10 Kg Digital, SRGS Pty Ltd, Lawnton Queensland Australia) and 200 kPa water pressure (measured using an in-line pressure gauge; HA3000, Holman, Osbourne Park, Western Australia), from a distance of no closer than 750 mm from the spray nozzle.

[169] Images were recorded using a Panasonic Lumix TZ30 or Canon 700D digital camera set to maximum image size, and photographing was completed and the samples returned to the water before the panels dried out to ensure the health of any adhered organisms.

[170] Depicted in Figures 15 and 16 are the films 1A and 1C after 294 and 295 days of immersion respectively. It can be seen that film 1A has provided effective broad spectrum anti-fouling protection in the sprayed area, with the surrounding unsprayed area showing substantial fouling attachment and growth. By contrast, film 1C shows a high level of fouling consistent with the embedded copper particles being encapsulated by the silicone polymer and no longer being in fluid communication with the surface (as also evident in Figure 14).

[171] Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is understood that the invention includes all such variations and modifications which fall within the spirit and scope of the present invention.

Claims

1. An anti-fouling covering, comprising:
 - a malleable film comprising at least a first layer of polymer; and
 - particles having anti-fouling properties embedded in a retentive matrix of the polymer, the particles discontinuously arranged in an embedment layer which comprises:
 - i) a surface population of the particles partially exposed on an anti-fouling surface of the anti-fouling covering; and
 - ii) a submerged population of the particles submerged in the matrix beneath the surface population of the particles,wherein the anti-fouling covering inhibits fouling of a fouling-prone surface covered by the covering, the particles of the submerged population contributing to fouling inhibition by fluidly communicating with the anti-fouling surface.
2. An anti-fouling covering according to claim 1, wherein the malleable film has a thickness of less than 1 mm.
3. An anti-fouling covering according to claim 1 or claim 2, wherein the particles have an average particle size of greater than 40 microns.
4. An anti-fouling covering according to claim 3, wherein the embedment layer has an average thickness of at least twice the average particle size.
5. An anti-fouling covering according to any one of claims 1 to 4, wherein the total loading of particles in the embedment layer is greater than 300 g/m².
6. An anti-fouling covering according to any one of claims 1 to 5, wherein the mass ratio of the particles to the polymer (g/g) is above 0.5 : 1.
7. An anti-fouling covering according to any one of claims 1 to 6, further comprising a substantially particle-free sublayer of the first layer of polymer beneath the embedment layer.

8. An anti-fouling covering according to any one of claims 1 to 6, wherein the embedment layer extends from the anti-fouling surface through the entire thickness of the first layer of polymer.
9. An anti-fouling covering according to any one of claims 1 to 8, wherein the malleable film further comprises a second polymeric layer adjacent to the first layer, the second polymeric layer having a Shore hardness greater than that of the polymer of the first layer.
10. An anti-fouling covering according to any one of claims 1 to 9, further comprising impact channels formed during embedment of the particles, wherein the particles of the submerged population contribute to fouling inhibition by fluidly communicating with the anti-fouling surface via the impact channels.
11. An anti-fouling covering according to claim 10, wherein at least some of the impact channels comprise a plurality of the particles.
12. An anti-fouling covering according to any one of claims 1 to 11, wherein the anti-fouling properties of the particles are provided by a chemical release mechanism.
13. An anti-fouling covering according to any one of claims 1 to 12, wherein the particles comprise a material selected from the group consisting of copper, zinc and compounds and alloys composed therefrom.
14. An anti-fouling covering according to any one of claims 1 to 13, further comprising an adhesive layer disposed on the malleable film for adhering to the fouling-prone surface.
15. An anti-fouling covering according to any one of claims 1 to 14, wherein the polymer is a thermoplastic polyurethane.
16. An anti-fouling covering according to any one of claims 1 to 15, on a release layer.

17. A method of producing an anti-fouling covering, the method comprising:

a) resiliently retaining a malleable film comprising at least a first layer of polymer against a backing surface; and

b) spraying a jet of particles having anti-fouling properties onto the first layer of polymer of the malleable film resiliently retained against the backing surface at a suitable impact velocity to embed the particles in a retentive matrix of the polymer, the particles thereby becoming discontinuously arranged in an embedment layer,

wherein the resilient retention against the backing surface inhibits disintegration of the malleable film upon impact by the particles.

18. A method according to claim 17, wherein the embedment layer comprises:

i) a surface population of the particles partially exposed on an anti-fouling surface of the anti-fouling covering; and

ii) a submerged population of the particles submerged in the matrix beneath the surface population of the particles.

19. A method according to claim 17 or claim 18, further comprising tensioning the malleable film before spraying the jet of particles onto the first layer of polymer.

20. A method according to any one of claims 17 to 19, wherein the malleable film is resiliently retained against the backing surface by a compression assembly, the compression assembly comprising an aperture through which the jet of particles is sprayed onto the first layer of polymer.

21. A method according to claim 20, wherein a width of the aperture is less than four times a width of the jet.

22. A method according to claim 20 or claim 21, wherein the compression assembly comprises a front clamping plate configured to press the malleable film against the backing surface, and the aperture is a slot in the front clamping plate.

23. A method according to claim 20 or claim 21, wherein the compression assembly comprises rollers configured to press the malleable film against the backing surface, and the aperture is a slot between the rollers.
24. A method according to claim 20 or claim 21, wherein spraying the jet of particles comprises traversing the jet along the length of the slot.
25. A method according to any one of claims 17 to 24, wherein the impact velocity is greater than 200 m/s.
26. A method according to any one of claims 17 to 25, further comprising:
- c) feeding the malleable film over the backing surface to expose unsprayed portions of the first layer of polymer; and
 - d) repeating steps a) and b).
27. A method according to any one of claims 17 to 26, wherein the malleable film has a thickness of less than 1 mm.
28. A method according to any one of claims 17 to 27, wherein the particles have an average particle size of greater than 40 microns.
29. An anti-fouling covering, produced by the method of any one of claims 17 to 28.
30. A method of protecting a fouling-prone surface against fouling, the method comprising covering the fouling-prone surface with the anti-fouling covering of any one of claims 1 to 16 or 29.
31. A method according to claim 30, wherein covering the surface comprises adhering or thermoforming the anti-fouling covering to the fouling-prone surface.
32. An apparatus for producing an anti-fouling covering, the apparatus comprising:
- a) a backing surface;

b) a retaining arrangement configured to resiliently retain a malleable film comprising at least a first layer of polymer against the backing surface; and

c) a spraying arrangement configured to spray a jet of particles having anti-fouling properties onto the first layer of polymer of the malleable film resiliently retained against the backing surface at a suitable impact velocity to embed the particles in a retentive matrix of the polymer.

33. An apparatus according to claim 32, further comprising:

d) a tensioning arrangement for tensioning the malleable film.

34. An apparatus according to claim 32 or claim 33, wherein the retaining arrangement comprises a compression assembly, the compression assembly comprising an aperture through which the jet of particles is sprayed onto the first layer of polymer.

35. An apparatus according to claim 34, wherein a width of the aperture is less than four times a width of the jet.

36. An apparatus according to claim 34 or claim 35, wherein the compression assembly comprises a front clamping plate configured to press the malleable film against the backing surface, and the aperture is a slot in the front clamping plate.

37. An apparatus according to claim 34 or claim 35, wherein the compression assembly comprises rollers configured to press the malleable film against the backing surface, and the aperture is a slot between the rollers.

38. An apparatus according to claim 36 or claim 37, further comprising a traversing arrangement for traversing the jet of particles along the length of the slot.

39. An apparatus according to any one of claims 32 to 38, wherein the spraying arrangement comprises a cold spray machine.

40. An apparatus according to any one of claims 32 to 39, further comprising:
- e) a feeder for feeding the malleable film over the backing surface to expose unsprayed portions of the first layer of polymer.

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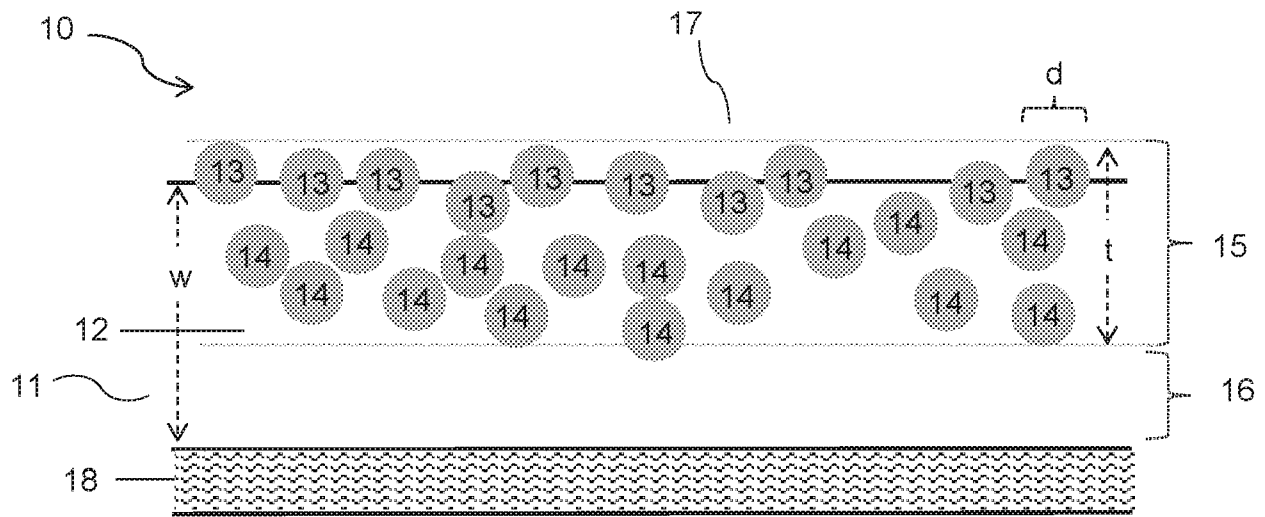


Figure 1

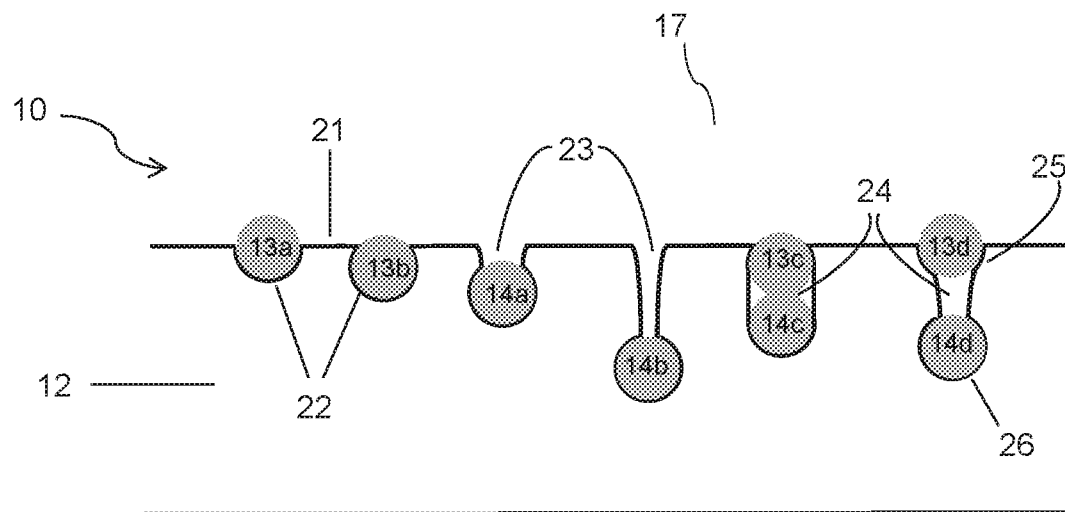


Figure 2

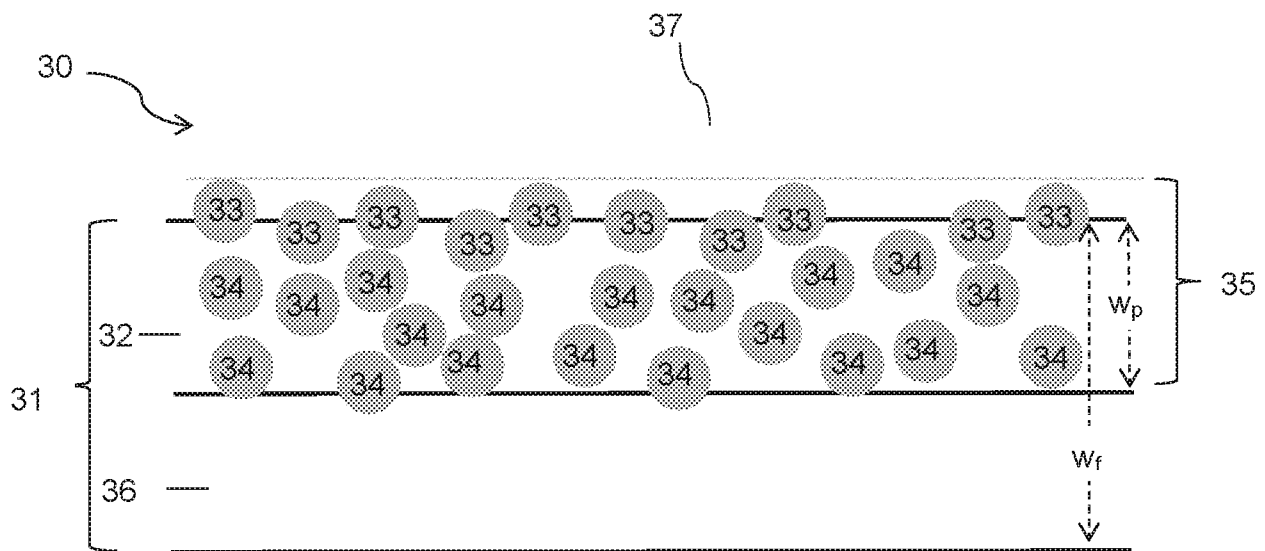


Figure 3

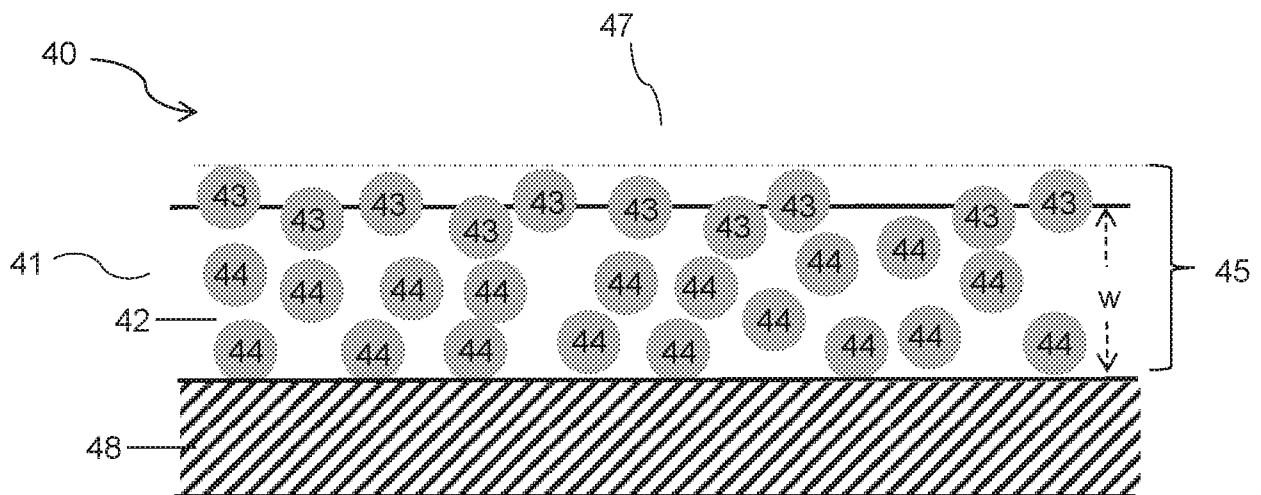


Figure 4

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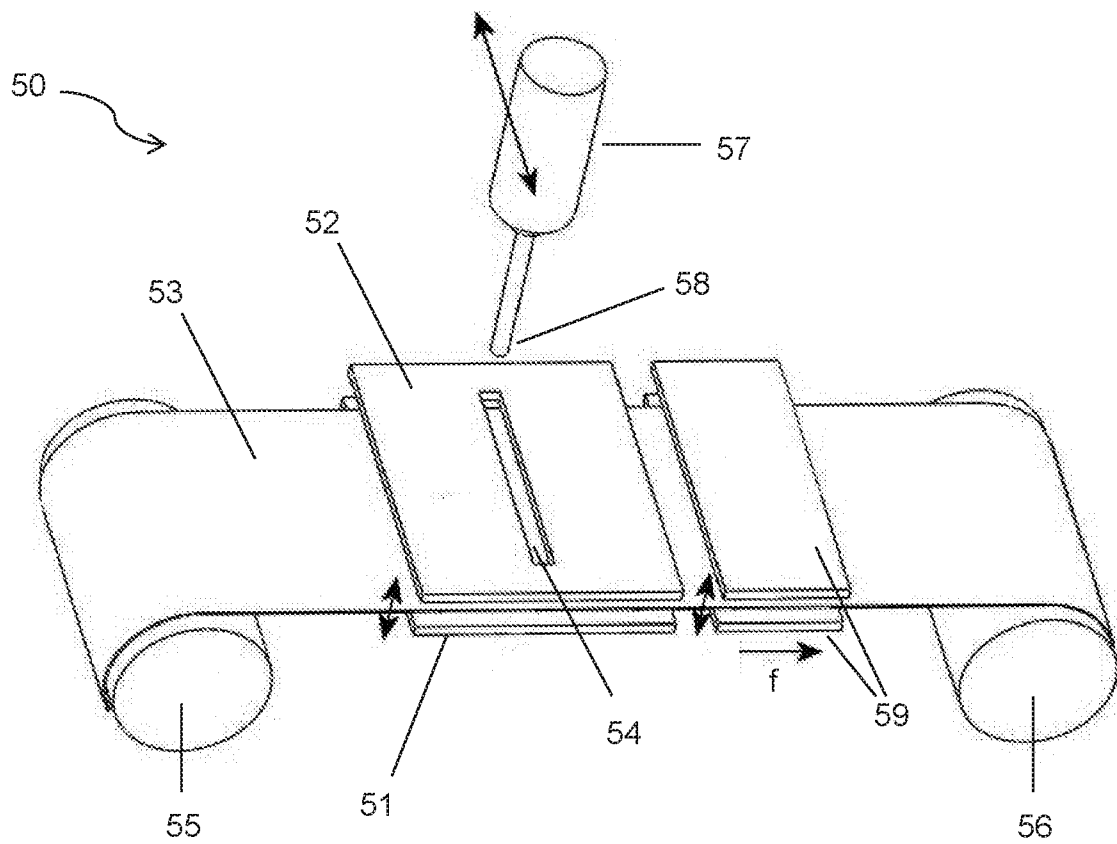


Figure 5

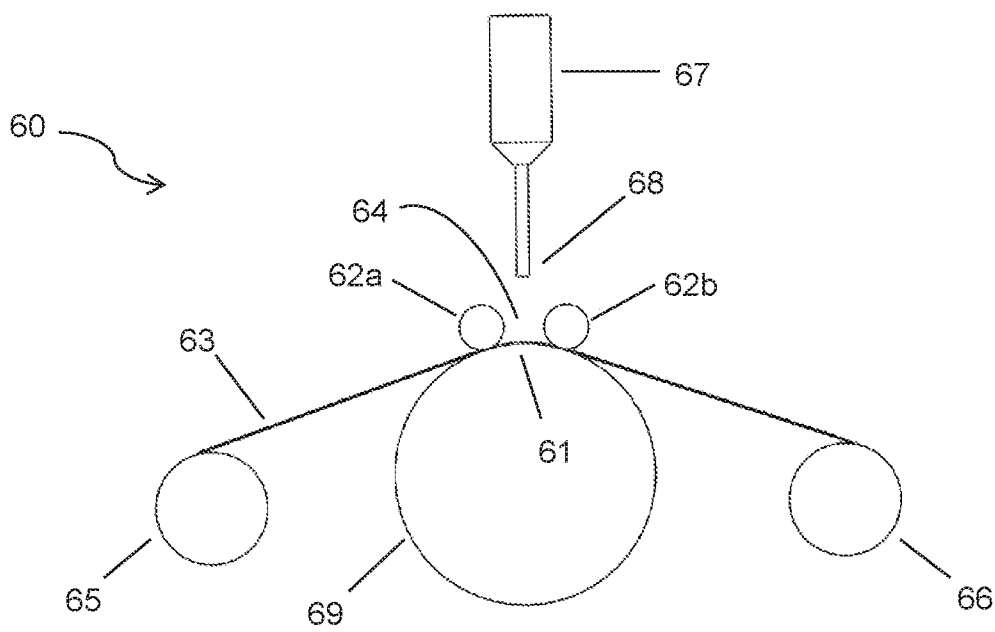


Figure 6

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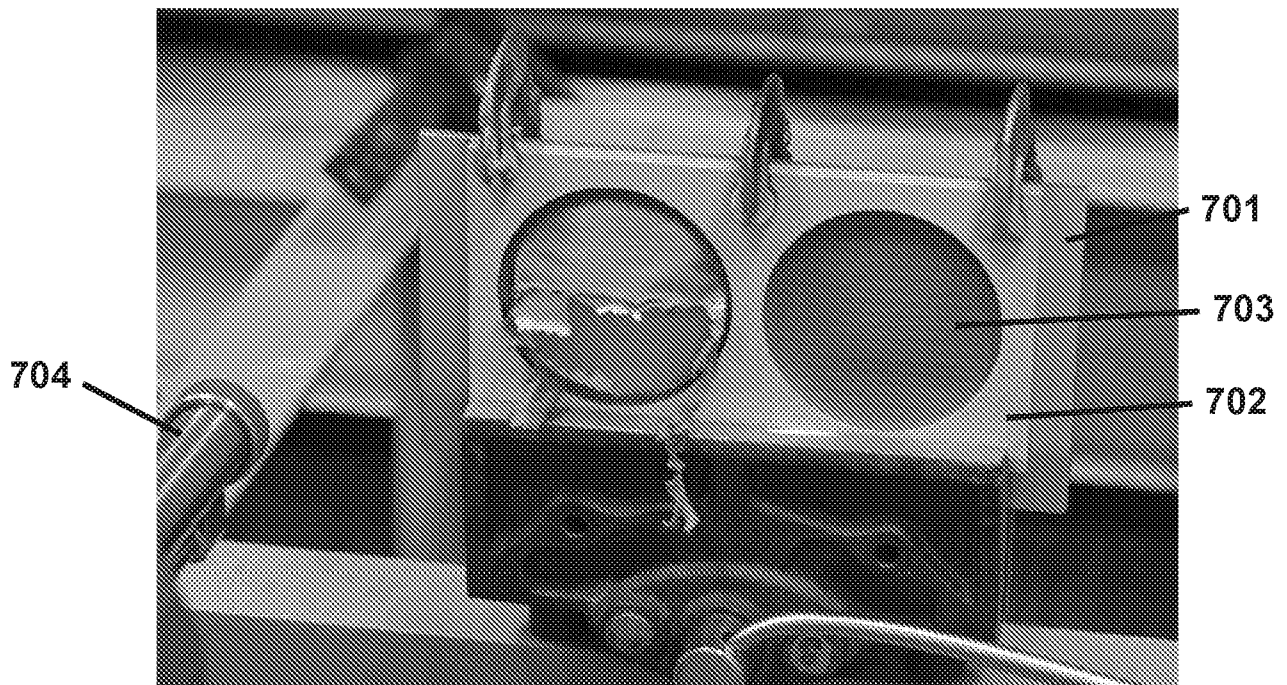


Figure 7

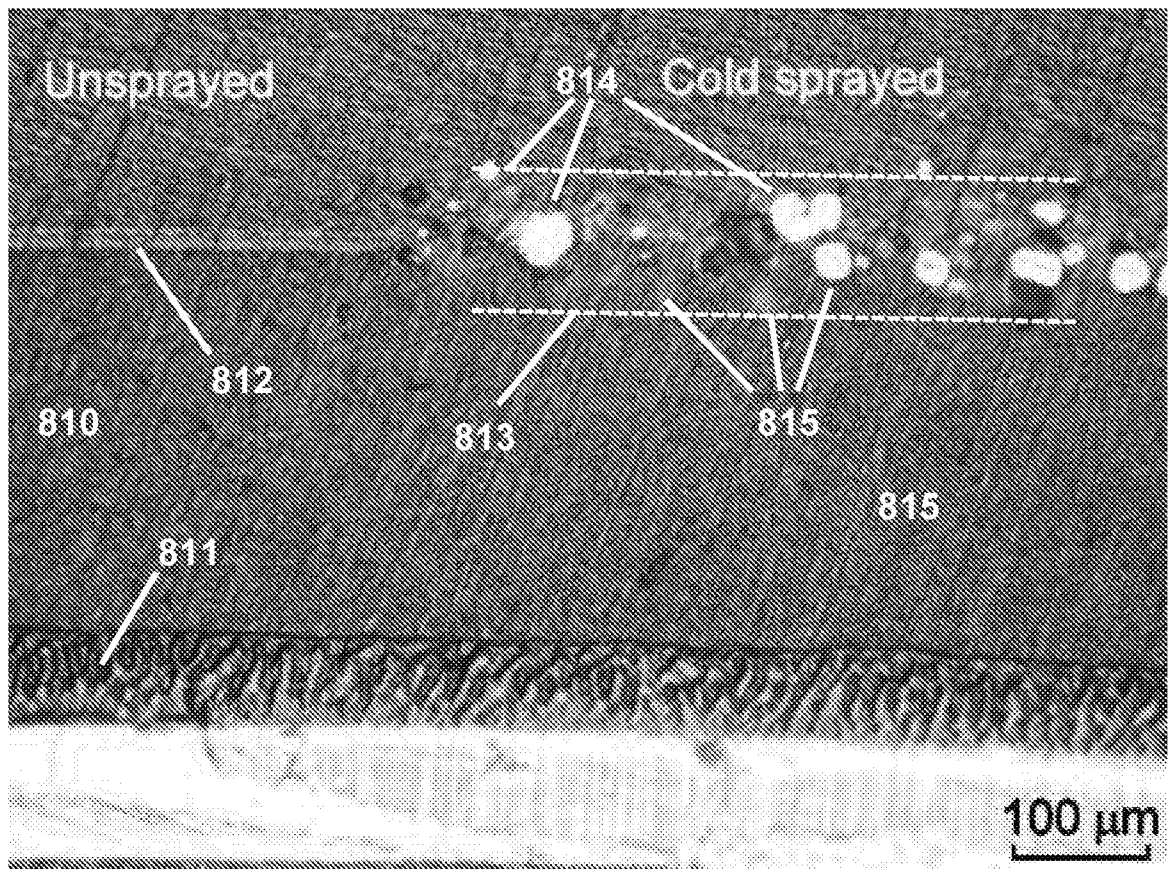


Figure 8

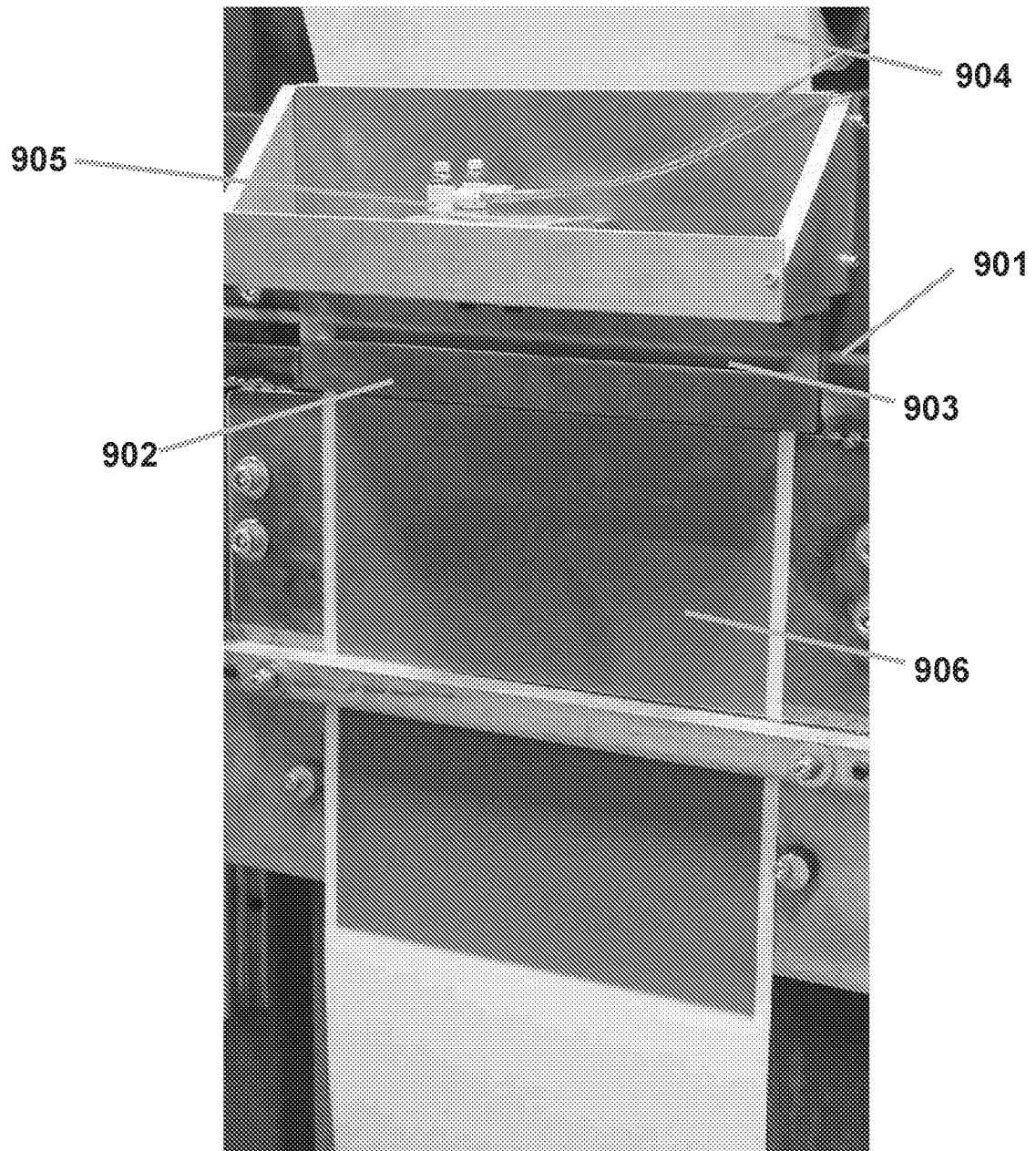


Figure 9

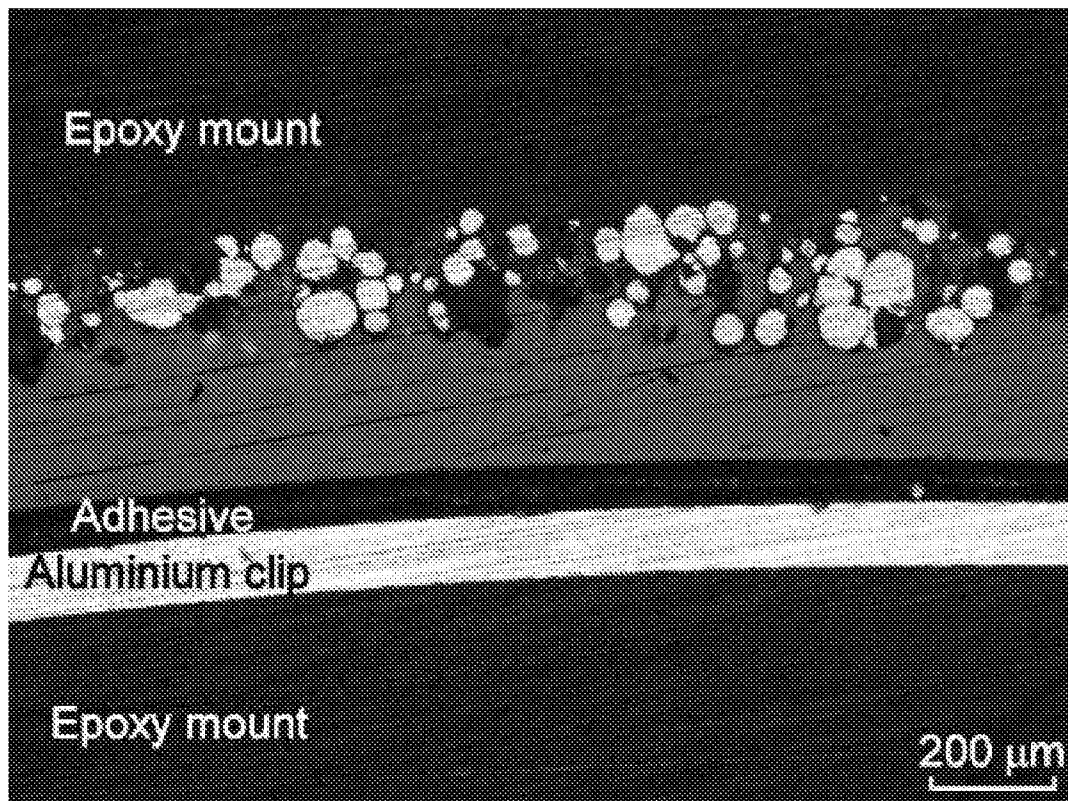


Figure 10

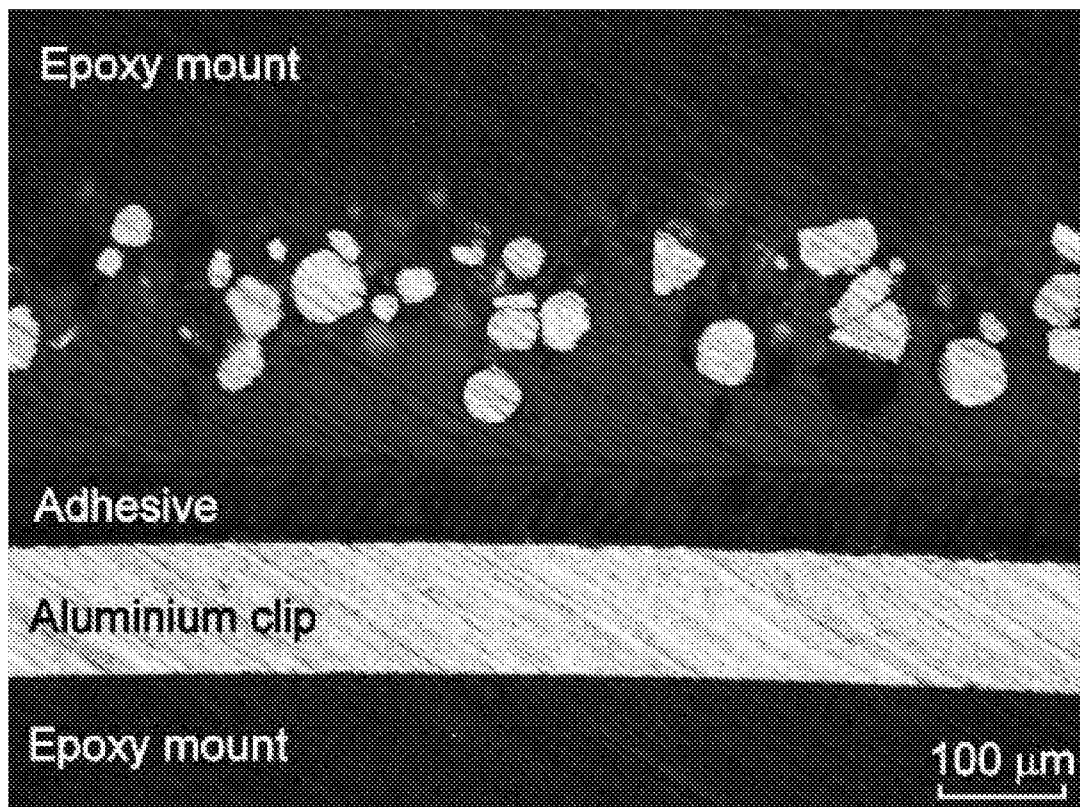


Figure 11

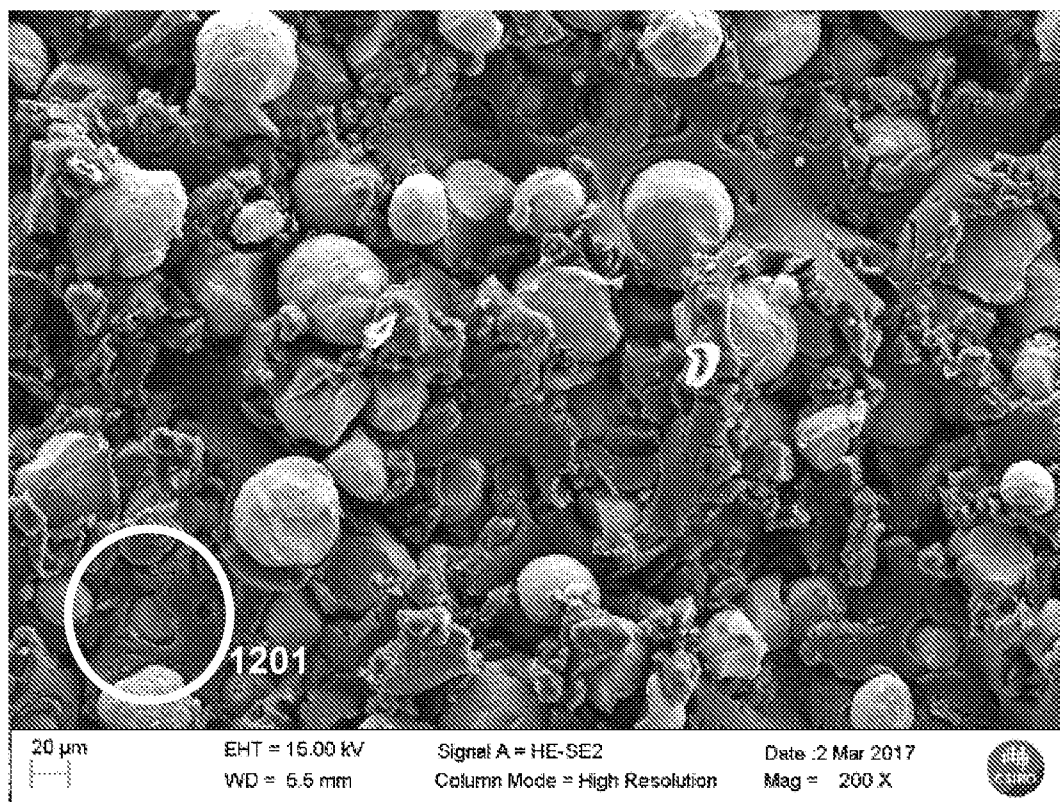


Figure 12

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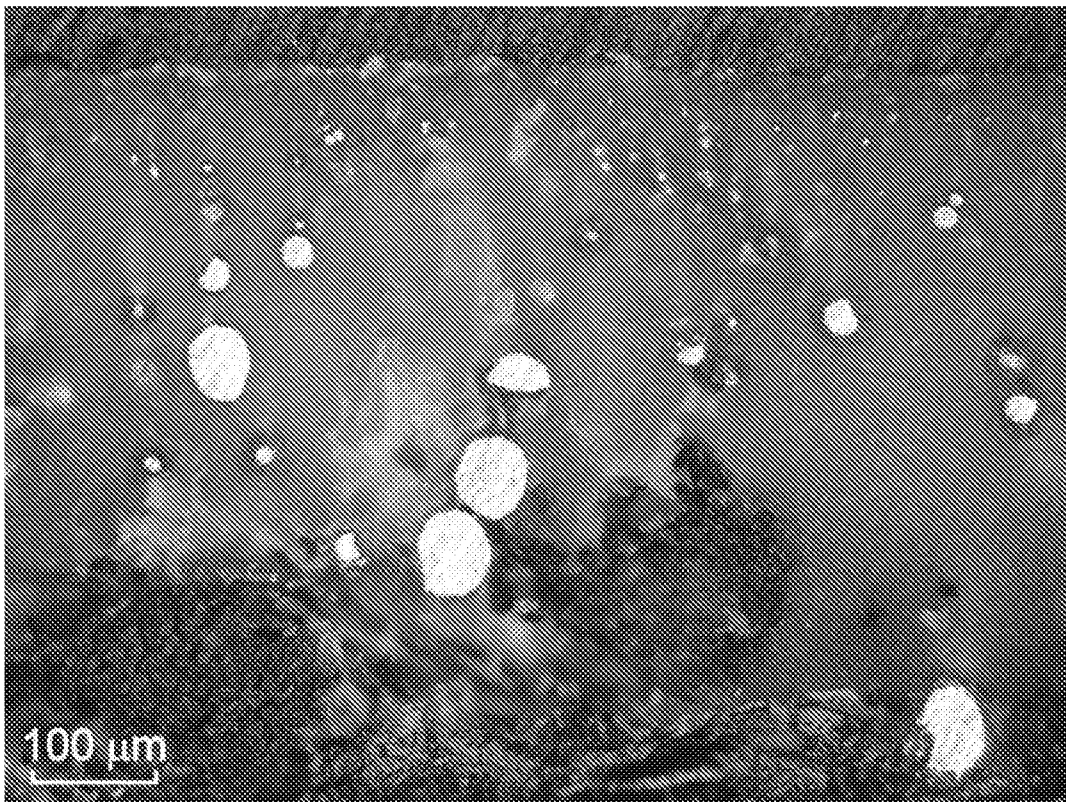


Figure 13

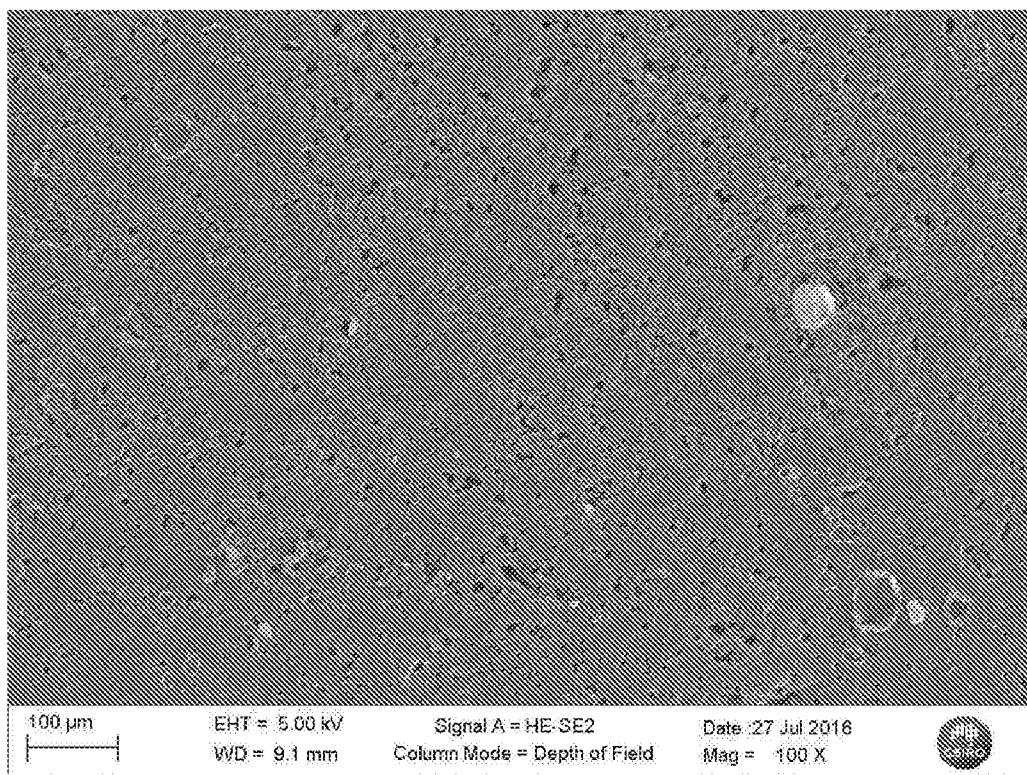


Figure 14

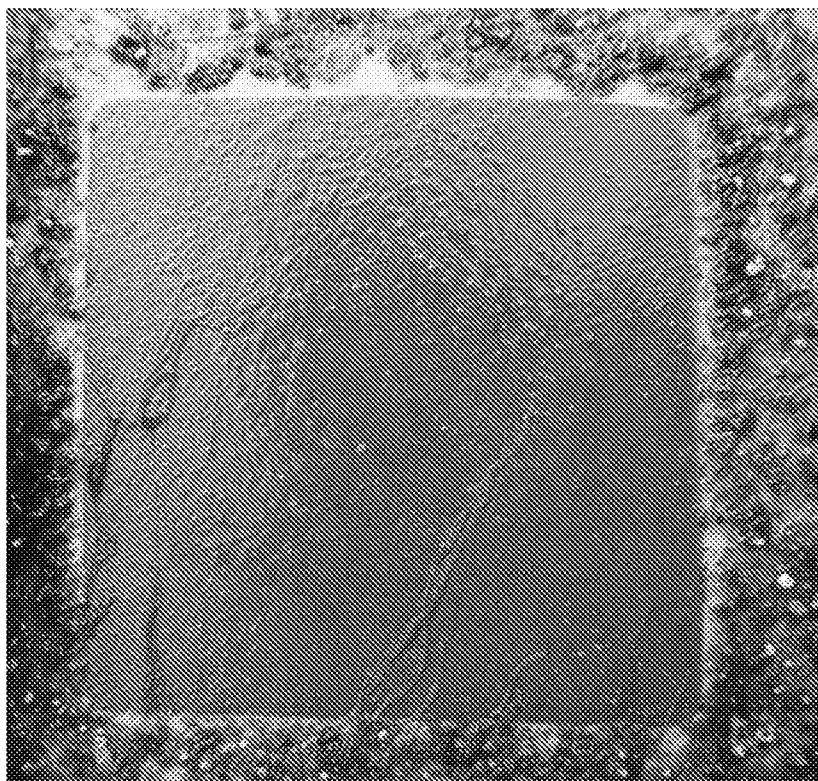


Figure 15

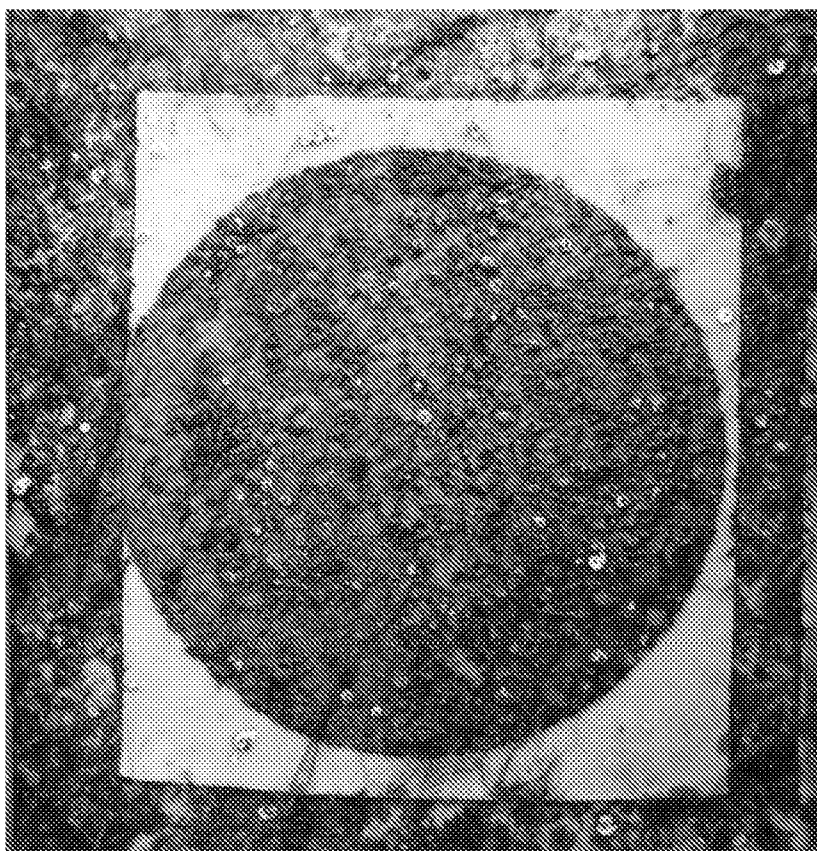


Figure 16

INTERNATIONAL SEARCH REPORT

 International application No.
PCT/AU2017/050586

A. CLASSIFICATION OF SUBJECT MATTER

C09D 5/16 (2006.01) C08J 7/04 (2006.01) B05D 1/12 (2006.01) C23C 24/04 (2006.01) B32B 15/00 (2006.01)

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)

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)

EPOQUE Search: Logical database PATENW (databases: EPODOC, WPIAP, TXPEA, TXPEB, TXPEC, TXPEE, TXPEF, TXPEH, TXPEI, TXPEP, TXPES, TXPW0EA, TXPUSE0A, TXPUSE1A, TXPUSEA, TXPUSEB, TXPEPEA, TXPEPEB) and private cluster KOSI15 (database: EPODOC, WPIAP) with following IPC/CPC class marks; (C08J7/04, C09D5/16, C08K3/08, C08K3/005, C08K2003/085, C08K2003/0862 OR C08K2003/0893, B32B15, B63B59/04) and Keywords (polymer, polyurethane, silicone, polyethylene, rubber, pvc, ptfе, anti-fouling, biocide, coating, layers, particles, submerge, embed, spray, jet, nozzle, atomise) and similar terms. Applicant/Inventors name searched in internal databases provided by IP Australia. ESPACENET AND GOOGLE Advanced Patent Search with above keywords.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	



Further documents are listed in the continuation of Box C



See patent family annex

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 18 August 2017	Date of mailing of the international search report 18 August 2017
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustalia.gov.au	Authorised officer Kosala Gunatillaka AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. +61262223652

INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/AU2017/050586
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 2014/0041905 A1 (INNOVA DYNAMICS, INC., [US]) 13 February 2014 Paragraphs [0015], [0087], [0096], [0102], [0106] - [0110], [0116], [0121] - [0125], [0137] - [0141], [0154], [0157] and claims 131 - 134 As above	1 - 3, 5, 6, 8 -16 7
X Y	US 2013/0236696 A1 (COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION [AU]) 12 September 2013 Claims 1 -3, 5 &15, paragraphs [0061], [0061], [0069], [0071] - [0074] and examples As above	1 - 6, 8 - 13, 15 7, 39
X Y	US 2005/0152869 A1 (WEED) 14 July 2005 Figures 1 & 6, paragraphs [0033], [0067] - [0070] , [0076] & [0097] and claims 12 - 13 As above	17 - 24, 27 - 38, 40 7, 25, 39
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A	US 2009/0169818 A1 (MICHEL) 02 July 2009 Abstract, Fig. 1 and claims 1 - 9	

INTERNATIONAL SEARCH REPORT		International application No.	
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INTERNATIONAL SEARCH REPORT		International application No.	
Information on patent family members		PCT/AU2017/050586	
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End of Annex			