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(54) Title: DIATOMS AS NATURAL CARRIERS FOR CONTROLLED RELEASE FOR METAL PROTECTION AND COATINGS

(57) Abstract: The present invention relates to a coating comprising a natural carrier for controlled release of a compound, such as for metal protection, a product comprising said coating or coating application, a method of modifying a natural carrier for controlled release, and methods of forming said coating or coating application, wherein the natural carrier is selected from exoskeletons of a Heterokontophyta species.



Diatoms as natural carriers for controlled release for metal protection and coatings

FIELD OF THE INVENTION

5 The present invention relates to a coating and coating application comprising a natural carrier for controlled release of a compound, such as for metal protection, a product comprising said coating or coating application, a method of modifying a natural carrier for controlled release, and
10 methods of forming said coating or coating application, wherein the natural carrier is selected from exoskeletons of a Heterokontophyta species.

BACKGROUND OF THE INVENTION

The present invention is in the field of said coating or
15 coating application.

Some major challenges faced when replacing toxic and carcinogenic Cr(VI)-based corrosion inhibitors by environmentally friendly ones are (i) reduction of negative inhibitor-coating matrix interactions that limit a novel
20 inhibitors efficiency, and (ii) control over release of the inhibitor in time. For this reason several encapsulation methods have been proposed in the last decade. The most common and successful concepts use 2D inorganic nanoparticles (e.g. montmorillonites, bentonites and hydrotalcites and more
25 recently 3D inorganic nanocarriers (e.g. zeolites and halloysites). Such carriers are considered to allow controlling inhibitor release by different mechanisms (e.g. diffusion, pH, redox, ion exchange) while at the same time prevent unwanted inhibitor reactions with e.g. a surrounding
30 polymer matrix and too fast inhibitor release leading to blistering. Despite significant progress and reported evidence for nanocarriers yielding protection of small damages (<100 µm width scratches) for short periods of immersion time, their long-term protection of relatively large damages is still
35 under question. Together with their limited versatility, often synthesis complexity, and insufficient local release capacity motivates the constant search for alternatives.

Diatoms are a major group of unicellular algae with the unique feature of forming highly ordered hollow nanoporous

silica exoskeletons (named frustules). Each of the estimated 100.000 extant species as well as the species found as mineral (diatomaceous earth) has a distinctive frustule (typically two symmetric sides hold together) which varies in size (from 2 μ m to 4 mm), shape and nanopore distribution and size. For their characteristics the diatom exoskeletons may be described as forming "pill-box" structures. The availability, morphological characteristics and potential application of fragmented bio-based diatom exoskeletons as carriers has recently attracted significant attention in the biomedical field where their use as drug delivery systems in fluid media has been studied.

Some prior art documents recite applications of microencapsulated biocides. WO 2010/148158 A1 recites a process for preparation of microencapsulated release biocidal actives and aqueous or solvent compositions thereof. Said document does not relate to a coating. EP 1 024 181 A1 recites an anti-corrosive coating and teaches to use large amounts of hollow filler, with therein inhibitors and anti-oxidants. Both documents relate to adsorption, i.e. only a surface is provided with a biocide or inhibitor, respectively.

The present invention therefore relates to and further aspects thereof, which overcomes one or more of the above disadvantages, without compromising functionality and advantages.

SUMMARY OF THE INVENTION

It is an object of the invention to overcome one or more limitations of the devices of the prior art and at the very least to provide an alternative thereto. The present invention relates to a coating, and likewise a coating application, comprising a natural carrier for controlled release of a compound, such as for metal protection, comprising 1-20 wt.%, preferably 2-19 wt.%, more preferably 3-18 wt.%, even more preferably 4-15 wt.%, such as 5-10 wt.%, of hollow structures, which may also be a halve structure, each structure enclosing an internal space thereof, wherein the hollow structures are selected from exoskeletons of a Heterokontophyta species, wherein the walls of the structure are mainly (e.g. 50-99.5 wt.%, such as 75-99 wt.%) of natural porous silica, wherein both the internal space and the surface of the hollow

structure is provided with 0.1-100 vol.%, preferably 0.2-80 vol.%, more preferably 0.5-50 vol.%, even more preferably 1-40 vol.%, such as 5-30 vol.%, of at least one of an organic and inorganic active compound, wherein wt.% and vol.% are based on a total weight of the coating and volume of the hollow structure, respectively. With the present method also hollow structures from a single (one) typically living species may be obtained, or of a limited number of such species. The term "active" may refer to "biologically active", "chemically active", "physically active", and combinations thereof, i.e. capable of acting or reacting as such or providing such activity. The amount of active compound may also be calculated on a weight/weight basis, and is typically in a range of 0.1-1000 g active compound/kg carrier, preferably 1/100 g/kg, such as 2-50 g/kg, typically also depending on a molar weight of the active compound. Contrary to the prior art both the internal space and the surface of the hollow structure may be provided with active compound. The natural carrier is formed by diatom species. The carrier is a hollow structure which is formed by the exoskeleton of said diatom species. The walls of the exoskeleton, and likewise if applicable the top and bottom (caps) are mainly of natural porous silica, and may contain further oxides, such as titanate. The hollow structures have an internal space, which internal space is provided (such as filled, doped) with an active compound, such as a corrosion inhibitor. The internal space may be largely or fully filled with said active compound (up to about 100 vol.%) or may be partly filled or even only slightly filled, depending on an application and/or intended use. The active compound may be organic and inorganic. Also combinations of active compounds are envisaged. The active compound may be present as such, or in a suitable solvent. The present coating or application therewith overcomes prior art and provides a controlled release of the active compound, especially in engineering applications, corrosion inhibition of underlying surfaces, such as in pipelines, aerospace coatings, coatings for bridge structures, in concrete applications, etc. The present diatoms can be used as carriers for the release of single or multiple chemical species to be released from the particles themselves

or for the particles embedded in bigger matrices such as coatings or concrete. The chemical species to be used can be broad in nature and can have different uses such as corrosion inhibition, self-healing, hydrophobicity, anti-biofouling, fire-retardant, anti-bacteria, anti-insects, colour restoration, lubricants, etc. The present coatings give fast and adequate protection that can be sustained long; in addition relatively large (mm-scale width/length) damages in coatings can be overcome or the effects thereof can at least be mitigated. A lower inhibitor-matrix interaction, a high local inhibitor storage, and a time-based release leading to sustained protection at damaged coated metals e.g. under immersion in salt solution is provided. The present exoskeletons comprising an active compound can be produced with ease, can comprise high amounts of active compound, can have complex architectures at a microscale, and relates to naturally formed products (including those grown in a bioreactor) being inherently environmentally friendly. The present coatings offer sufficient and constant supply of active compound, if applicable, and good release kinetics. The present nanoporous diatom algae exoskeletons allow for local inhibitor loading. In an example Cerium loaded exoskeletons show a fast diffusion controlled release. The Cerium loaded exoskeletons show long-term corrosion protection at damaged coatings. The Cerium loaded exoskeletons have comparable protection to the chromium based primer. Although the present invention has been proven for a cerium salt-epoxy-aluminium alloy system and a lithium salt-epoxy-aluminium alloy it is applicable to other inhibitor-coating-metal systems. It is possible to follow degradation processes of a damaged coating any electrochemical or optical technique designed to monitor corrosion processes such as scanning vibrating electrode technique or electrochemical impedance spectroscopy as well as other tools more common in industrial settings such as salt-fog spray.

In the present coating the active compound is at least one of a corrosion inhibitor, a self-healing compound, a compound for modifying surface tension (e.g. hydrophobicity or hydrophilicity), a precursor for a coating, an anti-bio

fouling compound, a fire-retardant, a bactericide, an insecticide, a colour restoration compound, an anti-icing agent, a de-icing agent, an anti-oxidant, a UV-protector, a lubricant, and an electrical conductor.

5 In the description the term "coating" is intended also to include "coating application", in so far as applicable.

In a second aspect the present invention relates to a product comprising the present coating or coating application, such as a pipeline, a platform, such as an off-shore platform,
10 an oil platform, a rocket/shuttle platform, an aerospace carrier, a vehicle, an automotive, an airplane, a train, a bridge, a bridge structure, and concrete.

In a third aspect the present invention relates to a method of modifying a natural carrier for controlled release,
15 such as for metal protection, comprising providing natural porous silica exoskeletons structures of a Heterokontophyta species, wherein the structures have an average height of 1 μm -5000 μm , an empty inner space with a cross section of 80 nm-49 μm , and pores in the exoskeleton with an average size of
20 5-100 nm, wherein the inner space and pores of the structures is provided with 0.1-100 vol.%, preferably 0.2-80 vol.%, more preferably 0.5-50 vol.%, even more preferably 1-40 vol.%, such as 5-30 vol.%, of at least one of an organic or inorganic active compound, such as an inhibitor selected from rare earth
25 salts, Li salts, etc., wherein the active compound is preferably also provided by precipitation on the surface.

In a fourth aspect the present invention relates to a method of forming a coating or coating application according to the invention. The coating may comprise a thermoset and/or
30 a thermoplast.

The present invention provides a solution to one or more of the above mentioned problems and overcomes drawbacks of the prior art.

The present invention is also topic of a scientific
35 article by S.J. Garcia et al., entitled "Cerium-loaded algae exoskeletons for active corrosion protection of coated AA2024-T3", which is submitted for publication, and which paper and contents and details thereof are incorporated by reference. Some of the paragraphs below relate closely to said article.

The paper provides various experimental results and characterizations of the present invention.

Advantages of the present description are detailed throughout the description.

5 DETAILED DESCRIPTION OF THE INVENTION

In an exemplary embodiment of the present coating the Heterokontophyta species may be an autotroph species, in particular a Bacillariophyceae, and more particular a diatomophyceae. The species can be readily grown in a
10 bioreactor.

In an exemplary embodiment of the present coating the exoskeleton may be naturally grown, obtained from diatomaceous earth, or produced in a bioreactor with extant diatom species. When obtained from diatomaceous earth smaller particles
15 typically need to be separated from the intact or largely intact exoskeletons; such may also be the case for naturally grown exoskeletons or those produced in a bioreactor, though to a lesser extent typically.

In an exemplary embodiment of the present coating the
20 naturally grown exoskeleton or the exoskeleton obtained from diatomaceous earth may be obtained by removing non-intact skeletons, such as by filtering, by mass-separation, or by settling, whereby a part or most, or even all, non-intact skeletons are removed, or wherein the exoskeleton produced in
25 the bioreactor may be obtained by removing organic matter from the diatom species, such as by heating. Therewith good control over and selection of e.g. a size distribution of exoskeletons is obtained.

In an exemplary embodiment of the present coating the
30 active compound may be at least one of phosphates, benzoates, silicates, vanadates, tungstates, zirconates, borates, molybdates, carbonic acids, amines, ketones, aldehydes, and heterocyclic compounds. Hence a large variety of active compounds may be applied, alone and in combination, amongst
35 others showing the versatility of the present coating.

In an exemplary embodiment of the present coating the corrosion inhibitor comprises one or more of a salt, such as an organic or inorganic salt, such as a rare earth salt, such as wherein the cation is Ce, Nd, La, Sc, or Dy, a Li-salt,

wherein the anion is one or more of NO₃⁻, alkyl phosphate, such as dibutyl phosphate, a thiol, a C(SH)=S comprising compound, and a carboxylate, such as diethyl dithiocarbamate, carbonate, etc.

5 In an exemplary embodiment of the present coating structures may have at least one of a cross section selected from circular, triangular, hexangular, square, rectangular, star-like, oval, and multiangular, such as octangular, an average height of 1 μm-5000 μm, preferably 10-1000 μm, such as 20-500
10 μm, an inner space with a cross section of 80 nm-49 μm, preferably 0.1-30 μm, such as 1-20 μm, and pores in the exoskeleton with an average size of 5-100 nm, such as 10-50 nm.

In an exemplary embodiment of the present coating
15 structures may be partly or fully capped, preferably fully capped. Such is a clear advantage as the inner space can then be filled fully or almost fully. Having partly or fully capped hollow structures typically implies a careful selection and/or growth method of exoskeletons.

20 In an exemplary embodiment of the present coating structures may be partly or fully provided with a partly or fully chemically modified surface. The present hollow structures can also comprise a modified surface. The surface may be modified before providing the active compound, after
25 providing the active compound, or during provision of the active compound. The surface may be fully modified or partly modified, such as providing an adequate amount of surface modifier. The surface may be chemically modified in a variety of ways providing various characteristics thereto.

30 In an exemplary embodiment of the present coating the active compound may be provided by precipitation on the surface.

In an exemplary embodiment the present coating may comprise 5-99 wt.%, preferably 10-95 wt.%, more preferably 15-90 wt.%,
35 even more preferably 20-80 wt.%, such as 50-75 wt.%, of at least one of a polymer of an epoxy resin, a phenolic resin, a polyurethane, a polyester, a polyamide, a polyimide, a silicone, an alkyd resin, an amino resin, and combinations thereof. It is an important advantage that the present hollow

structures can be provided in small amounts, thereby leaving the characteristics of coatings largely unaltered. In fact the addition of the present hollow structures may in this respect be regarded as a provision of a small amount of additive to the coating.

In an exemplary embodiment of the present coating the exoskeleton particle size distribution may be a Gaussian-shaped size distribution. In view of using the present particles such offers advantages in controllable characteristics of the coating.

In an exemplary embodiment of the present coating the standard deviation in particle size may be very limited, such as wherein $3\sigma < (3 \times \text{average exoskeleton particle size})$, preferably $3\sigma < (2 \times \text{average exoskeleton particle size})$, more preferably $3\sigma < (1 \times \text{average exoskeleton particle size})$, such as preferably $3\sigma < (0.5 \times \text{average exoskeleton particle size})$ or (for larger particle sizes ($>20\mu\text{m}$) preferably $3\sigma < (0.1 \times \text{average exoskeleton particle size})$.

In an exemplary embodiment of the present coating an average exoskeleton particle may be from 1-100 μm , preferably 5-50 μm , more preferably 10-20 μm , such as 12-15 μm . Such uniform and small particle sizes are found to be beneficial to the present coatings.

In an exemplary embodiment the present coating may comprise 2-20 Heterokontophyta species, i.e. a limited number of species with well-defined characteristics, preferably 3-12 species, such as 5-10 species, each species having a different average size. For instance a first species may have an average size of 5 μm , a second species of 15 μm , and a third species of 50 μm . It is preferred to have size distributions that are not overlapping, for instance in view of final characteristics of a coating, i.e. that within e.g. 3σ two adjacent size distributions do not overlap. Such is very well achievable with the present structures as very well defined structures may be obtained, especially when obtained from species grown in a bioreactor.

In an exemplary embodiment the present coating may comprise >99% intact hollow structures, preferably > 99.5%, such as >

99.9%, based on a total number of species; i.e. practically no broken structures are present. Such is especially achievable with the living species grown in a bioreactor. For comparison, structures obtained in mining typically may have up to 50% broken structures, which percentage could be lowered with big efforts to 20%, and with even more effort to 5% or slightly lower.

The present coating can be applied to a large number and variety of products.

In an exemplary embodiment the present method of modifying a natural carrier for controlled release, such as for metal protection, may comprise providing natural porous silica exoskeletons structures of a Heterokontophyta species, wherein the structures have an average height of 1 μm -5000 μm , an empty inner space with a cross section of 80 nm-49 μm , and pores in the exoskeleton with an average size of 5-100 nm, wherein the inner space and pores of the structures is provided with 0.1-100 vol.% of at least one of an organic or inorganic active compound. The modifying method may comprise further steps. For instance the present carrier may be separated, such that largely intact exoskeletons are obtained. Separation may e.g. be performed by suspending exoskeletons in a solvent, treating the suspension, such as by sonification, such that larger and smaller particles are spatially separated, removing the smaller typically not-intact particles, such as by decanting, and repeating the steps as often as required to obtain a full separation, such as 2-10 times, typically 3-7 times. Thereafter an optional post-treatment on the obtained exoskeletons may be performed, or a combination of post-treatment steps. For instance an acid treatment may be performed, such as by providing a 1-5M acid, such as H_2SO_4 , and mixing at room temperature at 50-500 rpm, such as 100-200 rpm, for a period of 1-24 hrs, such as 2-16 hrs, thereby removing impurities, such as metal species. Thereafter the exoskeletons are typically washed with water, and dried, such as at 40-80 $^{\circ}\text{C}$, typically at 50-60 $^{\circ}\text{C}$, during 2-48 hrs, such as 12-24 hrs. Likewise an alkaline treatment may be performed using a 10^{-1} - 10^{-4} M, such as 10^{-3} M alkaline solution, such as NaOH, during 1-3 hrs, such as 1.5 hrs, and

further following the steps mentioned above. Also a combination of an acid and alkaline post-treatment may be performed.

5 In an exemplary embodiment the present method of modifying a natural carrier for controlled release the active compound may be provided by ion exchange, typically after structural modification of the exoskeleton.

10 In a further aspect the present invention may relate to a method of forming the present coating or coating application comprising providing 1-20 wt.% of a hollow structure enclosing an internal space thereof, wherein the walls of the hollow structure is at least one natural porous silica exoskeleton of a Heterokontophyta species, wherein the internal space and the surface of the hollow structure is provided with 0.1-100 vol.%
15 of at least one of an organic and inorganic active compound, providing 5-99 wt.% of at least one of an uncured polymer, mixing the hollow structures and uncured polymer, applying the mixed polymer to a surface, and curing the polymer, wherein wt.%/vol.% are based on a total weight/volume of the
20 coating/hollow structure.

In a further aspect the present invention may relate to a method of forming the present coating or coating application comprising providing 1-20 wt.% of a hollow structure enclosing an internal space thereof, wherein the walls of the hollow
25 structure is at least one natural porous silica exoskeleton of a Heterokontophyta species, wherein the internal space and the surface of the hollow structure is provided with 0.1-100 vol.% of at least one of an organic and inorganic active compound, providing 5-99 wt.% of at least one of a thermoplastic polymer
30 in a solvent, mixing the hollow structures and polymer, such as by extrusion, applying the mixed polymer to a surface, and increasing the temperature, wherein wt.%/vol.% are based on a total weight/volume of the coating/hollow structure.

The method of forming the present coating may further
35 comprises providing 1-40 wt.% of a hollow structure enclosing an internal space thereof, preferably 2-30 wt.%, more preferably 5-20 wt.%, such as 10-15 wt.%, wherein the walls of the hollow structure is at least one natural porous silica exoskeleton of a Heterokontophyta species, wherein the

exoskeleton is produced in a bioreactor, wherein both the internal space and the surface of the hollow structure is provided with 0.1-100 vol.% of at least one of an organic and inorganic active compound. It has been found that especially for exoskeletons produced in a bioreactor much high loadings of filler can be provided to coatings with a more controlled particle size and property distribution.

In view of changes in the coating the present use of exoskeletons and embedded inhibitors is found to lead to a clear decrease in inhibitor-polymer chemical interactions, such as can be seen in a strong decrease in yellowing in the case of Ce-loaded exoskeletons in an epoxy matrix. Figure 6 shows microscope images of (a-b) Cerium Nitrate and (c-d) Ce-DE mixed with Ancamine®2500 just after mixing (a, c) and after 1 hour (b, d). Images illustrate the yellowing process in the case of the salt-amine couple and its absence in the case of the Ce-DE amine one. Image confirms the strong reduction of the yellowing when the Ce-salt is included in an exoskeleton nanoporous micro particle.

The invention will hereafter be further elucidated through the following examples which are exemplary and explanatory of nature and are not intended to be considered limiting of the invention. To the person skilled in the art it may be clear that many variants, being obvious or not, may be conceivable falling within the scope of protection, defined by the present claims.

FIGURES

Figure 1 shows a set of SEM images and EDX spectra of the diatom exoskeletons before (1a and 1c) and after (1b and 1c) the purification process as well as the particle size distribution (1d).

Figure 2. (a) SEM image of a single fractured diatom exoskeleton after corrosion inhibitor. (b) Comparative XRD spectra of DE, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ corrosion inhibitor salt, and Ce-DE.

Figure 3. Cerium release kinetics of cerium nitrate from the salt powder (top-line) and from the Ce-DE particles (bottom-line) obtained with a real-time UV/VIS spectroscopy from the 252nm wavelength.

Figure 4a-d. SEM (a) and EDS micrographs for C (b), Ce (c) and Si(d) of the fractured plane of an epoxy coating loaded with Ce-DE.

Figure 5. Microscope images of polished AA2024-T3 before, during, and after 7 days of immersion in 0.05M NaCl (a) without corrosion inhibitor (b) 0.05mM $\text{Ce}(\text{NO}_3)_3$ and (c) Ce-doped DE containing 0.05 mM $\text{Ce}(\text{NO}_3)_3$. Note, images during immersion do not represent real sizes due to the distortion by the solution.

Figure 6. Microscope images of (a-b) Cerium Nitrate and (c-d) Ce-DE mixed with Ancamine®2500 just after mixing (a, c) and after 1 hour (b, d).

DETAILED DESCRIPTION OF FIGURES

The figures are further detailed throughout the description.

EXPERIMENTS

The present invention is demonstrated for an epoxy-amine coating on an aerospace aluminium alloy AA2024-T3 system. Cerium nitrate was used as the corrosion inhibitor giving an excellent corrosion inhibition in the copper-rich aluminium alloy. Cerium nitrate was here stored into refined diatomaceous earth (DE) and its loading, release kinetics and corrosion inhibition efficiency of bare AA2024-T3 in salt solution. These systems were studied by real-time UV/VIS spectroscopy, SEM/EDS and Raman spectroscopy. The active corrosion protection of the cerium-loaded DE particles (Ce-DE) was then evaluated in a particle-loaded epoxy coating by an in-situ hyphenated opto-electrochemical device after creating highly controlled scratches of 130 μm width at the bottom of the scratch. The results obtained are compared to those obtained for an unloaded epoxy coating and two epoxy coatings directly loaded with cerium nitrate and potassium dichromate respectively. The in-situ hyphenated opto-electrochemical approach allowed for obtaining real-time optical and electrochemical information on the corrosion/protection processes. The analysis of the results showed a clear delay of the on-set and kinetics of the degradation process when the Ce-DE were used reaching protective values similar to those of the chromium-based system for the studied conditions. The involvement of the cerium ions on the corrosion inhibition was

further confirmed by a post-mortem analysis of the damaged site by SEM-EDS and Raman spectroscopy. While the protection offered by the inhibiting species was detected with both techniques, the higher spatial resolution of the Raman signal at the scratch gained additional information on the interaction between cerium species and copper-rich intermetallic phases. The results here presented prove active corrosion protection of coated metal structures.

Materials and preparation

Diatomaceous earth Diafil 525 mainly consisting of cylinder shaped diatom exoskeletons was supplied by Profiltr Customized Solutions (NL). The as-received diatomaceous earth consists of 89.0 wt. % amorphous silica (SiO_2), a tapped powder bulk density of 0.42 g/cm^3 and a mean particle size of $12 \mu\text{m}$. Cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) with >99% purity were purchased from Sigma-Aldrich. Commercial 2 mm thick bare AA2024-T3 sheet obtained from Kaizer Aluminium was used as metallic substrate. Commercially available bisphenol-A based epoxy resin (Epikote[™] 828) and amine cross linker (Ancamine[®]2500) were supplied by AkzoNobel (NL) and used as received to form the coating binder. Xylene with a purity of 99% was used as epoxy solvent. All aqueous solutions for the particle doping, corrosion and release studies were prepared using Millipore[®] Elix 3 UV filtered water.

Refining of the as-received diatomaceous earth

In order maximize the amount of intact diatom exoskeletons and reduce the impurities content (i.e. non-silica) a refining process was applied. Therein 8.0 g of as-received diatomaceous earth was suspended in 120 ml demineralized water and sonicated for 30 min. This was left in unstirred condition for 30 min to allow the silica intact exoskeletons to settle down. The supernatant (containing the impurities and small diatom parts) was discarded with the help of a glass pipette. This settling process was repeated 5 times (without sonication). Finally the settled particles were filtered using a Whatman[®] grade 595 paper filter and dried in a vacuum oven at 60°C for 24 h. The refined diatomaceous earth, referred to as "DE", was used in the rest of the study as the corrosion inhibitor

carrier.

Post-treatment of DE

DE may be post-treated in order to remove impurities. Almost all impurities can thereby be removed. The treated DE shows a somewhat better behaviour, e.g. in terms of release of active compound over time and in amount.

For acid treatment, 200 mg refined DE was dispersed in 20ml solution of 3.0M Sulfuric acid (H_2SO_4) using a 50ml flask fitted with a condenser and controlled at 100 in an oil bath. The flask was fitted with magnetic stirrer at around 200 rpm. After 16 hours the content was filtered using a Whatman® grade 595 paper filter. The acid treated product was repeatedly washed with water until the filtrate reached a pH of 7. The residue was removed from the filter and dried in a vacuum oven at 60°C for 24 hours to completely dry.

For alkaline treatment, two batches were used. Namely, 200mg refined DE for the first batch and 200 mg acid treated DE for the second batch. This was mixed with 5.0 ml of sodium hydroxide solution (NaOH) having a pH of 11. The content was magnetically stirred for 1.5 hours at 200 rpm in a 50 ml flask. Finally the diatoms were filtered and water cleaned with the use of a Whatman® grade 595 paper filter until the filtrate reached a pH of 7. The residue was removed from the filter and dried in a vacuum oven at 60°C for 24 hours to completely dry.

DE doping with cerium nitrate

For the doping procedure a powder mixture of 0.85 g refined DE and 0.15 g cerium nitrate hexahydrate was added to 2.0 ml demineralized water. The mixture was then placed on a shaking table at 320 rpm for 24 h followed by complete drying in an oven at 80 °C under ambient atmosphere for another 24 h. As a result of the process a DE powder containing 15 wt. % of cerium nitrate was obtained. The loaded powder was then screened through a stainless steel sieve of 50 µm aperture to reduce agglomerates and conform the here on called cerium-doped DE (Ce-DE).

Coatings preparation

AA2024-T3 metal sheets were cut into pieces of 25x50 mm prior to surface modification and coating application. The

metal surface preparation consisted of the following sequential steps: (i) removal of native oxide layer and surface chemistry homogenization using SiC sandpapers down to grit 320; (ii) surface roughness formation by Scotch Brite 3M "Clean N Finish grade AVFN"; (iii) degreasing with acetone; and (iv) immersion in a 2M NaOH aqueous solution for 10 seconds followed by rinsing with distilled water and air drying in order to increase the surface OH fraction and therefore adhesion with the subsequent organic coating.

The organic coatings were prepared using a mixture of Epikote™ 828, Ancamine®2500 and Xylene (2.70:1.57:1 weight ratio). Five coating systems were formulated as summarized in Table 1. In all cases the epoxy-amine-xylene mixture was first high-shear mixed for 5 minutes at 2500 rpm in a high-speed mixer. In order to reduce possible side reactions with the epoxy/amine matrix the mixtures were then let pre-cure at ambient conditions for 30 min before the corrosion inhibiting components (cerium nitrate powder, DE, Ce-DE or potassium dichromate) were added. The mixtures were then manually stirred to form a homogeneous mixture, applied on the AA2024-T3 coupons by a 100µm spiral bar coater and cured at 60°C for 24h as reported elsewhere to achieve complete crosslinking. After curing the coated panels were stored in a desiccator until 30 min before testing. The final pigment volume concentration (PVC) in the dry coatings could be calculated.

Table 1. Overview of the coatings compositions, sample coding and relevant coating parameters.

Coating (epoxy- amine based)	Particle content (wt. % over binder)	Thickness (µm)	PVC (%)	Active inhibitor content (moles/kg binder)
E	None	110±20	0	0
DE	Refined DE: 12	80±20	25	0
Ce	As received Ce(NO ₃) ₃ : 2	80±20	0.5	0.04
Ce-DE	Ce loaded DE: 14	110±20	25	0.04

Cr	As received $K_2Cr_2O_7$: 2	100±20	0.8	0.06
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Coatings damage formation for corrosion inhibition evaluation

Reproducible and controlled 5 mm long and 130 μ m wide scratches (at the bottom of the scratch) were created on the coated panels with a CSM Microscratch tester using a 100 μ m Rockwell C diamond tip in multi-pass mode. For this, the tip was programmed to give 5 passes at each load of 5N, 10N and 15N at the same location until the AA2024-T3 substrate was reached.

Details of testing methods and equipment used are given in the above mentioned publication.

Cerium interaction with the exposed AA2024-T3 metal surface

In order to confirm the involvement of cerium in the active corrosion protection at damage sites both SEM-EDS and Raman spectroscopy analysis were performed at the scribe bottom (metal) of the damaged coated samples used in the opto-electrochemical study. For the Raman analysis a Renishaw inVia reflex microscope equipped with a research-grade Leica microscope objective at 50 $\times$ magnification and numerical aperture of 0.55 was used. A 532-nm laser light with an effective laser power of 32mW in 1 second excitation measurements was employed. Control tests were performed on a copper block, cerium oxide precipitates, and on bare AA2024-T3 exposed to inhibited and non-inhibiting solutions.

Particle and coating characterization

Figure 1 shows a set of SEM images and EDX spectra of the diatom exoskeletons before (1a and 1c) and after (1b and 1d) the purification process as well as the particle size distribution (1d). From the SEM images it becomes clear that the purification process significantly reduced the amount of broken diatoms and other impurities of the as received diatomaceous earth as intended. The SEM inserts in Figures 1a and 1b further confirm the removal of very small particles blocking the nano-pores in the as-received exoskeletons. The particle size analysis showed a near Gaussian-shaped size distribution with an increased peak centred at 12 μ m (Figure 1d) as well as a drop of the small fraction particles after the purifying process. Here four clearly different diatom

species were present with mainly sp. *Aulacoseira* species having a cylindrical pill-box structure with nanopores of around 500nm evenly distributed around the exoskeleton wall.

EDX analysis was used to determine the effect of the purification process on the removal of the chemical species different than the silica of the diatom shell. Figure 1c shows the predominance of silicon (Si) and oxygen (O) constituents as expected for diatom silica (SiO_2) exoskeletons. Small traces of aluminium (Al), Iron (Fe), Calcium (Ca) and Magnesium (Mg) were also detected and assigned to impurity oxides (Al_2O_3 , Fe_2O_3 , CaCO_3 , CaO , and MgO). The purifying process used was not capable of fully removing oxide impurities. The presence of the impurities in the clean DE did not have an effect on the ulterior cerium doping when the doping procedure proposed in this work was employed. As the impurities did not have a significant effect in the doping it was decided to skip the acid and alkali post-treatments to simplify the process.

Diatom exoskeleton loading with corrosion inhibitors was confirmed by SEM and XRD analysis (Figure 2). The XRD spectra in Figure 2b show that the DE (refined diatomaceous earth) primarily consisted of amorphous silica with some minor diffraction peaks at 22.0° and 26.6° corresponding to crystalline structures of quartz and cristobalite. The XRD spectra for the Ce-DE (cerium doped DE) shows the amorphous silica baseline combined with crystalline peaks corresponding to $\text{Ce}(\text{NO}_3)_3$. The increased intensity of the peaks compared to pure $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ is presumably caused by the decrease of water in the crystal lattice due to drying and localized deposition on the diatom silica surface. The results confirm that, during the doping process, the cerium inhibitor did not change its crystalline structure and remained as an inorganic salt primarily inside the diatom exoskeletons body space and nanopores, thereby confirming the success of the developed doping procedure.

Figure 3 shows a difference in release behaviour (dissolution and diffusion) of the $\text{Ce}(\text{NO}_3)_3$ salt directly placed in a paper filter of an UV-Vis system and that of the cerium salt contained in the Ce-DE particles. By analysing the

release plots it is possible to realize that the filter paper influenced the dissolution of the inhibitor by delaying its release. The release response for both systems is comparable whereby the release at the beginning increases exponentially due to the high solubility of $\text{Ce}(\text{NO}_3)_3$ and ends asymptotically. Interestingly, the release curve for the Ce-DE particles is slower than that of the cerium salt over the entire time domain. The increasing separation in time between the two release curves plotted against $t^{1/2}$ shows that there may not be a single 'trapping' time for the cerium but an entire spectrum delayed between 10 and 10^3 seconds with respect to the cerium salt in the filter. These results confirmed that the cerium inhibitor loaded in the DE structure was able to come out by a time diffusion controlled process in aqueous solution as intended.

The active corrosion protection by the release of cerium from the Ce-DE particles in solution was studied by a detailed SEM/EDS and Raman study on bare AA2024-T3 immersed in 0.05M NaCl solutions. Despite the delay with respect to the salt, the results confirmed a sufficiently fast cerium release from the DE particles enough to prevent local corrosion by the formation of protective cerium precipitates at copper-rich phases.

Figure 4 shows the SEM-EDS micrograph of a fractured epoxy coating containing Ce-DE particles. The fractured plane shows a DE cylindrical particle (from the top) embedded in the epoxy matrix. The EDS analysis further confirmed the presence of high cerium concentrations inside the exoskeleton with a low carbon signal of the polymeric matrix thereby confirming the cerium inhibitor remained in the inner volume of the DE when the Ce-DE particles were mixed with the epoxy coating. This is a critical requirement of the localized long term corrosion protection.

Corrosion inhibition

Formation of corrosion products and local corrosion sites are found at the scribe of the non-inhibited coatings (Epoxy and DE). On the other hand, both the Ce-DE coating and the Chromium containing coating (Cr) do not show significant

variations with the immersion time at the scribe, indicating active corrosion protection of the damaged site.

Figure 5(a) shows that pitting corrosion on AA2024 occurs within the first 3h of immersion in 0.05 M NaCl, indicating the susceptibility to localized corrosion in salt water for this alloy. The initiation of pitting did not occur when 0.05mM $\text{Ce}(\text{NO}_3)_3$ or Ce-doped DE was added, as shown in Figure M(b-c), confirming that the Ce-doped DE is actively protecting the substrate. DE particles were visible at the aluminium surface during the immersion-test for the Ce-doped DE solution after 3h. Furthermore, several secondary phases became visible at the surface after 7 days of immersion and rinsing with water.

For the quantitative analysis three main characteristic parameters were used, (1) Relative variation of the total impedance in time, (2) Open circuit potential (OCP), and (3) The degraded area around the scratch with immersion time. Upon studying these parameters results were found to be satisfactory.

Conclusions

A new biobased carrier for corrosion inhibition is introduced. The use of diatom algae silica exoskeletons, provides protection of AA2024-T3 structures by cerium nitrate corrosion inhibitor. Corrosion protection levels comparable to those given by a coating containing potassium dichromate were obtained. High protection levels are achieved, a reduction of unwanted reactions, a high inhibitor storage in the silica cages and the fast and sustained release of the cerium inhibitor at the damaged site. Also protective systems based on fast release and inhibition at damaged sites followed by a time-sustained or on-demand release of corrosion inhibitors supplied at a sufficient concentration to ensure the long term protection are envisaged. The use of inhibitor loaded algae exoskeleton particles for sustained corrosion inhibition here presented is not restricted to cerium and epoxy coatings on aluminium substrates but should be regarded as being generic with a high versatility and potential for developing environmentally friendly active corrosion protection in coated metals.

CLAIMS

1. Coating comprising a natural carrier for controlled release of a compound, such as for metal protection, comprising

1-20 wt.% of hollow structures, each structure enclosing an internal space thereof, wherein the hollow structures are selected from exoskeletons of at least one Heterokontophyta species, wherein the walls of the structure are mainly of natural porous silica,

wherein both the internal space and the surface of the hollow structure is provided with 0.1-100 vol.% of at least one of an organic and inorganic active compound, wherein the active compound is at least one of a corrosion inhibitor, a self-healing compound, a compound for modifying surface tension, a precursor for a coating, an anti-bio fouling compound, a fire-retardant, a bactericide, an insecticide, a colour restoration compound, an anti-icing agent, a de-icing agent, an anti-oxidant, a UV-protector, a lubricant, and an electrical conductor,

wherein wt.% and vol.% are based on a total weight of the coating and volume of the hollow structure, respectively.

2. Coating according to claim 1, comprising 2-19 wt.% hollow structures.

3. Coating according to any of the preceding claims, wherein the Heterokontophyta species is an autotroph species, in particular a Bacillariophyceae, and more particular a diatomophyceae.

4. Coating according to any of the preceding claims, wherein the exoskeleton is naturally grown, obtained from diatomaceous earth, or produced in a bioreactor with extant diatom species.

5. Coating according to claim 4, wherein the naturally grown exoskeleton or the exoskeleton obtained from diatomaceous earth is obtained by removing non-intact skeletons, or wherein the exoskeleton produced in the bioreactor is obtained by removing organic matter from diatom species, such as by heating.

6. Coating according to claim 5, wherein the exoskeleton

is obtained by removing non-intact skeletons, or wherein the exoskeleton is obtained by removing organic matter from diatom species by heating.

7. Coating according to any of the preceding claims, wherein the active compound is at least one of a phosphate, a benzoate, a silicate, a vanadate, a tungstate, a zirconate, a borate, a molybdate, a carbonic acid, an amine, a ketone, an aldehyde, and a heterocyclic compound.

8. Coating according to any of the preceding claims, wherein the corrosion inhibitor comprises one or more of a salt.

9. Coating according to claim 8, wherein in the salt the cation is selected from Ce, Nd, La, Sc, Dy, and Li, and the anion is one or more of NO_3^- , alkyl phosphate, such as dibutyl phosphate, a thiol, a $\text{C}(\text{SH})=\text{S}$ comprising compound, and a carboxylate, such as diethyl dithiocarbamate.

10. Coating according to any of the preceding claims, wherein structures have at least one of a cross section selected from circular, triangular, hexangular, octangular, square, rectangular, star-like, oval, and multiangular, an average height of 1 μm -5000 μm , an inner space with a cross section of 80 nm-49 μm , and pores in the exoskeleton with an average size of 5-100 nm.

11. Coating according to any of the preceding claims, wherein structures are partly or fully capped.

12. Coating according to any of the preceding claims, wherein structures are partly or fully provided with a partly or fully chemically modified surface.

13. Coating according to any of the preceding claims, wherein the active compound is provided by precipitation on the surface.

14. Coating according to any of the preceding claims, comprising 5-99 wt.% thermoset and/or thermoplast.

15. Coating according to any of the preceding claims, comprising 5-99 wt.% of at least one of a polymer of an epoxy resin, a phenolic resin, a polyurethane, a polyester, a polyamide, a polyimide, a silicone, an alkyd resin, an amino resin, and combinations thereof.

16. Coating according to any of the preceding claims,

wherein an exoskeleton particle size distribution is a Gaussian-shaped size distribution.

17. Coating according to claim 16, wherein 3σ (standard deviation) $< (3 \times \text{average exoskeleton particle size})$.

5 18. Coating according to claim 16 or 17, wherein an average exoskeleton particle is from 1-100 μm .

19. Coating according to any of the preceding claims, comprising 2-20 Heterokontophyta species, each species having a different average size.

10 20. Coating according to any of the preceding claims, comprising $>99\%$ intact hollow structures.

21. Product comprising a coating according to any of the preceding claims, wherein the product is selected from a pipeline, an aerospace carrier, a platform, an off-shore
15 platform, an oil platform, a rocket/shuttle platform, a vehicle, an automotive, an airplane, a train, a bridge, a bridge structure, and concrete.

22. Method of modifying a natural carrier for controlled release, comprising
20 providing natural porous silica exoskeletons structures of a Heterokontophyta species,
wherein the structures have an average height of 1 μm -5000 μm , an empty inner space with a cross section of 80 nm-49 μm , and pores in the exoskeleton with an average size of 5-100 nm,
25 wherein both the inner space and pores of the structures is provided with 0.1-100 vol.% of at least one of an organic or inorganic active compound, wherein the active compound is at least one of a corrosion inhibitor, a self-healing compound, a compound for modifying surface tension, a precursor for a
30 coating, an anti-bio fouling compound, a fire-retardant, a bactericide, an insecticide, a colour restoration compound, an anti-icing agent, a de-icing agent, an anti-oxidant, a UV-protector, a lubricant, and an electrical conductor.

23. Method according to claim 22, wherein the active
35 compound is provided by ion exchange.

24. Method according to claim 22 or 23, wherein the exoskeletons structures are pre-treated and post-treated, wherein treatment is selected from at least one of refining, washing, drying, purifying, filtering, fractioning, acid

treatment, and alkaline treatment.

25. Method of forming a coating according to any of claims 1-20, comprising

providing 1-20 wt.% of a hollow structure enclosing an
5 internal space thereof, wherein the walls of the hollow structure is at least one natural porous silica exoskeleton of a Heterokontophyta species,

wherein both the internal space and the surface of the hollow structure is provided with 0.1-100 vol.% of at least one of an
10 organic and inorganic active compound, wherein the active compound is at least one of a corrosion inhibitor, a self-healing compound, a compound for modifying surface tension, a precursor for a coating, an anti-bio fouling compound, a fire-retardant, a bactericide, an insecticide, a colour restoration
15 compound, an anti-icing agent, a de-icing agent, an anti-oxidant, a UV-protector, a lubricant, and an electrical conductor,

providing 5-99 wt.% of at least one of an uncured polymer or
20 5-99 wt.% of at least one of a thermoplastic polymer in a solvent,

mixing the hollow structures and uncured polymer or polymer, applying the mixed polymer to a surface, and curing the polymer or increasing the temperature.

26. Method according to claim 25, wherein mixing the
25 hollow structures and polymer is by extrusion.

27. Method according to claim 25 or 26, further comprising providing 1-40 wt.% of a hollow structure enclosing an internal space thereof, wherein the walls of the hollow structure is at least one natural porous silica exoskeleton of
30 a Heterokontophyta species, wherein the exoskeleton is produced in a bioreactor, wherein both the internal space and the surface of the hollow structure is provided with 0.1-100 vol.% of at least one of an organic and inorganic active compound.

AMENDED CLAIMS

received by the International Bureau on 30 July 2018 (30.07.2018)

1. Coating comprising a natural carrier for controlled release of a compound, comprising

5 1-20 wt.% of hollow structures, each structure enclosing an internal space thereof, wherein the hollow structures are selected from exoskeletons of at least one Heterokontophyta species, wherein the walls of the structure are mainly of natural porous silica,

10 wherein both the internal space and the surface of the hollow structure is provided with 0.1-100 vol.% of at least one of an organic and inorganic active compound, wherein the compound is at least one of biologically active, chemically active, and physically active, wherein the active compound is at least one
15 of a corrosion inhibitor, a self-healing compound, a compound for modifying surface tension, a precursor for a coating, an anti-bio fouling compound, a fire-retardant, a bactericide, an insecticide, a colour restoration compound, an anti-icing agent, a de-icing agent, an anti-oxidant, a UV-protector, a lubricant,
20 and an electrical conductor, wherein wt.% and vol.% are based on a total weight of the coating and volume of the hollow structure, respectively.

2. Coating according to claim 1, comprising 2-19 wt.% hollow structures.

25 3. Coating according to any of the preceding claims, wherein the Heterokontophyta species is an autotroph species, in particular a Bacillariophyceae, and more particular a diatomophyceae.

30 4. Coating according to any of the preceding claims, wherein the exoskeleton is naturally grown, obtained from diatomaceous earth, or produced in a bioreactor with extant diatom species.

35 5. Coating according to claim 4, wherein the naturally grown exoskeleton or the exoskeleton obtained from diatomaceous earth is obtained by removing non-intact skeletons, or wherein the exoskeleton produced in the bioreactor is obtained by removing organic matter from diatom species.

6. Coating according to claim 5, wherein the exoskeleton is obtained by removing non-intact skeletons, or wherein the exoskeleton is obtained by removing organic matter from diatom

species by heating.

7. Coating according to any of the preceding claims, wherein the active compound is at least one of a phosphate, a benzoate, a silicate, a vanadate, a tungstate, a zirconate, a borate, a molybdate, a carbonic acid, an amine, a ketone, an aldehyde, and a heterocyclic compound.

8. Coating according to any of the preceding claims, wherein the corrosion inhibitor comprises one or more of a salt.

9. Coating according to claim 8, wherein in the salt the cation is selected from Ce, Nd, La, Sc, Dy, and Li, and the anion is one or more of NO_3^- , alkyl phosphate, a thiol, a $\text{C}(\text{SH})=\text{S}$ comprising compound, and a carboxylate.

10. Coating according to any of the preceding claims, wherein structures have at least one of a cross section selected from circular, triangular, hexangular, octangular, square, rectangular, star-like, oval, and multiangular, an average height of $1\text{ }\mu\text{m}$ - $5000\text{ }\mu\text{m}$, an inner space with a cross section of 80 nm - $49\text{ }\mu\text{m}$, and pores in the exoskeleton with an average size of 5 nm - 100 nm .

11. Coating according to any of the preceding claims, wherein structures are partly or fully capped.

12. Coating according to any of the preceding claims, wherein structures are partly or fully provided with a partly or fully chemically modified surface.

13. Coating according to any of the preceding claims, wherein the active compound is provided by precipitation on the surface.

14. Coating according to any of the preceding claims, comprising 5-99 wt.% thermoset and/or thermoplast.

15. Coating according to any of the preceding claims, comprising 5-99 wt.% of at least one of a polymer of an epoxy resin, a phenolic resin, a polyurethane, a polyester, a polyamide, a polyimide, a silicone, an alkyd resin, an amino resin, and combinations thereof.

16. Coating according to any of the preceding claims, wherein an exoskeleton particle size distribution is a Gaussian-shaped size distribution.

17. Coating according to claim 16, wherein 3σ (standard deviation) $< (3 \times \text{average exoskeleton particle size})$.

18. Coating according to claim 16 or 17, wherein an average exoskeleton particle is from 1-100µm.

19. Coating according to any of the preceding claims, comprising 2-20 Heterokontophyta species, each species having a
5 different average size.

20. Coating according to any of the preceding claims, comprising >99% intact hollow structures.

21. Product comprising a coating according to any of the preceding claims, wherein the product is selected from a
10 pipeline, an aerospace carrier, a platform, an off-shore platform, an oil platform, a rocket/shuttle platform, a vehicle, an automotive, an airplane, a train, a bridge, a bridge structure, and concrete.

22. Method of modifying a natural carrier for controlled
15 release, comprising providing natural porous silica exoskeletons structures of a Heterokontophyta species, wherein the structures have an average height of 1 µm-5000 µm, an empty inner space with a cross section of 80 nm-49 µm, and
20 pores in the exoskeleton with an average size of 5-100 nm, wherein both the inner space and pores of the structures is provided with 0.1-100 vol.% of at least one of an organic or inorganic active compound, wherein the active compound is at least one of a corrosion inhibitor, a self-healing compound, a
25 compound for modifying surface tension, a precursor for a coating, an anti-bio fouling compound, a fire-retardant, a bactericide, an insecticide, a colour restoration compound, an anti-icing agent, a de-icing agent, an anti-oxidant, a UV-protector, a lubricant, and an electrical conductor.

30 23. Method according to claim 22, wherein the active compound is provided by ion exchange.

24. Method according to claim 22 or 23, wherein the exoskeletons structures are pre-treated and post-treated, wherein treatment is selected from at least one of refining,
35 washing, drying, purifying, filtering, fractioning, acid treatment, and alkaline treatment.

25. Method of forming a coating according to any of claims 1-20, comprising providing 1-20 wt.% of a hollow structure enclosing an internal

space thereof, wherein the walls of the hollow structure is at least one natural porous silica exoskeleton of a Heterokontophyta species,

wherein both the internal space and the surface of the hollow structure is provided with 0.1-100 vol.% of at least one of an organic and inorganic active compound, wherein the active compound is at least one of a corrosion inhibitor, a self-healing compound, a compound for modifying surface tension, a precursor for a coating, an anti-bio fouling compound, a fire-retardant, a bactericide, an insecticide, a colour restoration compound, an anti-icing agent, a de-icing agent, an anti-oxidant, a UV-protector, a lubricant, and an electrical conductor,

providing 5-99 wt.% of at least one of an uncured polymer or 5-99 wt.% of at least one of a thermoplastic polymer in a solvent, mixing the hollow structures and uncured polymer or polymer, applying the mixed polymer to a surface, and curing the polymer or increasing the temperature.

26. Method according to claim 25, wherein mixing the hollow structures and polymer is by extrusion.

27. Method according to claim 25 or 26, further comprising providing 1-40 wt.% of a hollow structure enclosing an internal space thereof, wherein the walls of the hollow structure is at least one natural porous silica exoskeleton of a Heterokontophyta species, wherein the exoskeleton is produced in a bioreactor, wherein both the internal space and the surface of the hollow structure is provided with 0.1-100 vol.% of at least one of an organic and inorganic active compound.

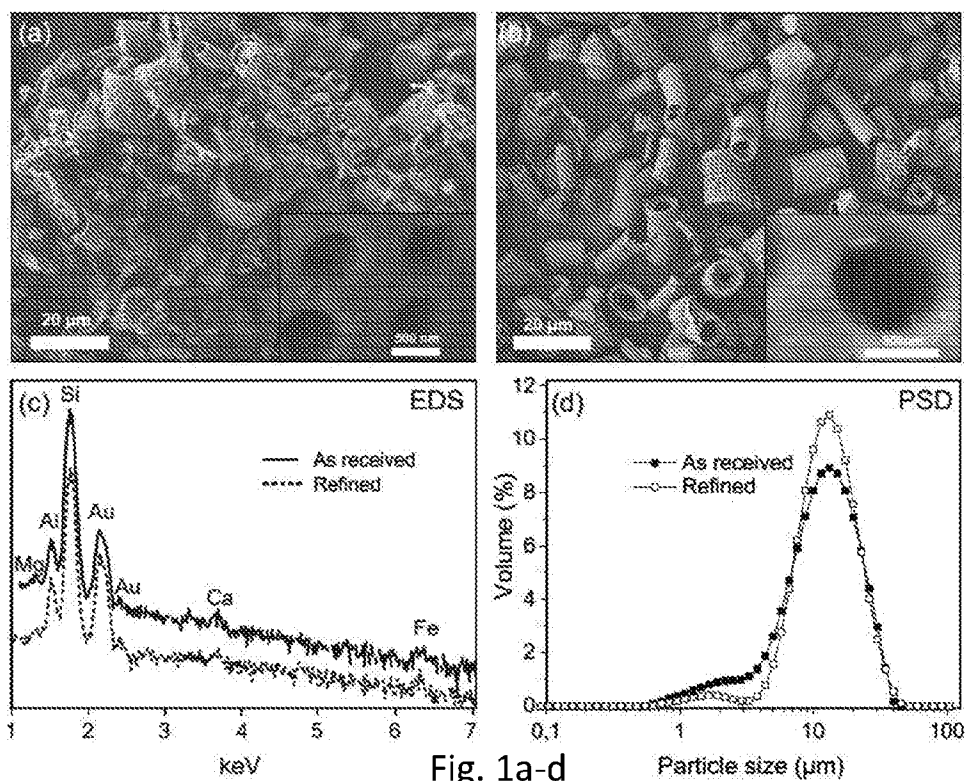


Fig. 1a-d

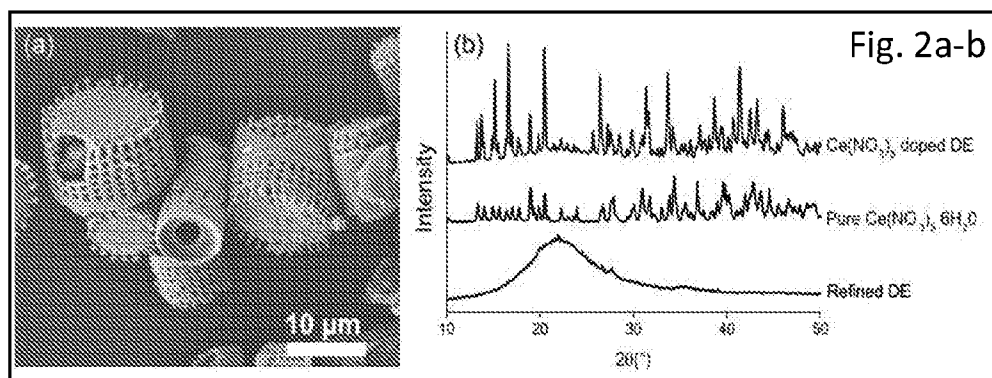


Fig. 2a-b

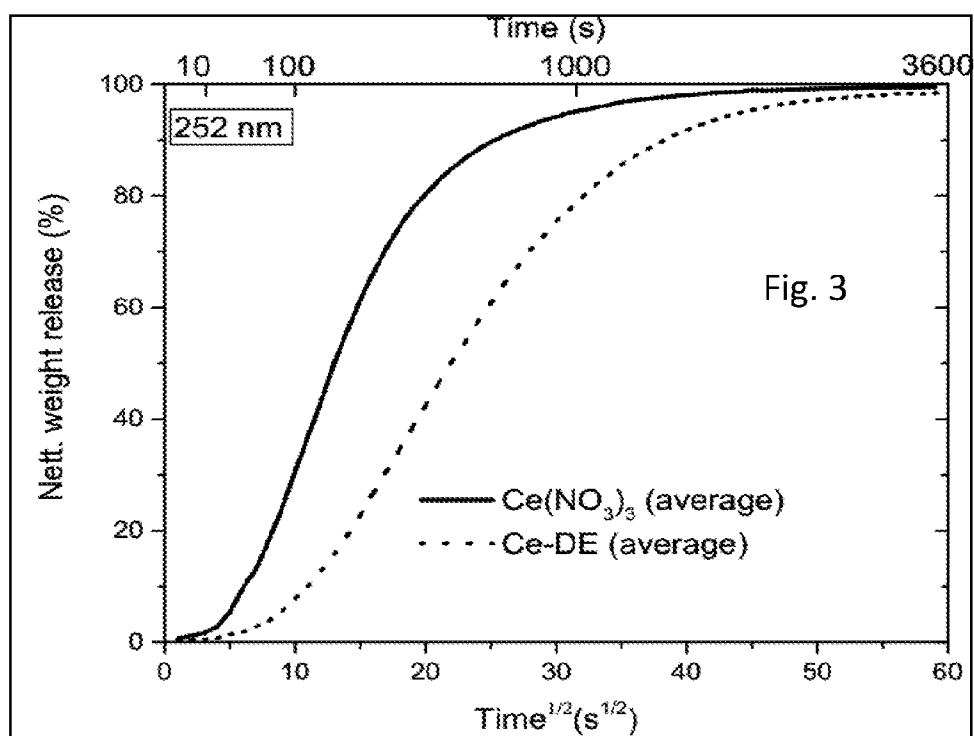
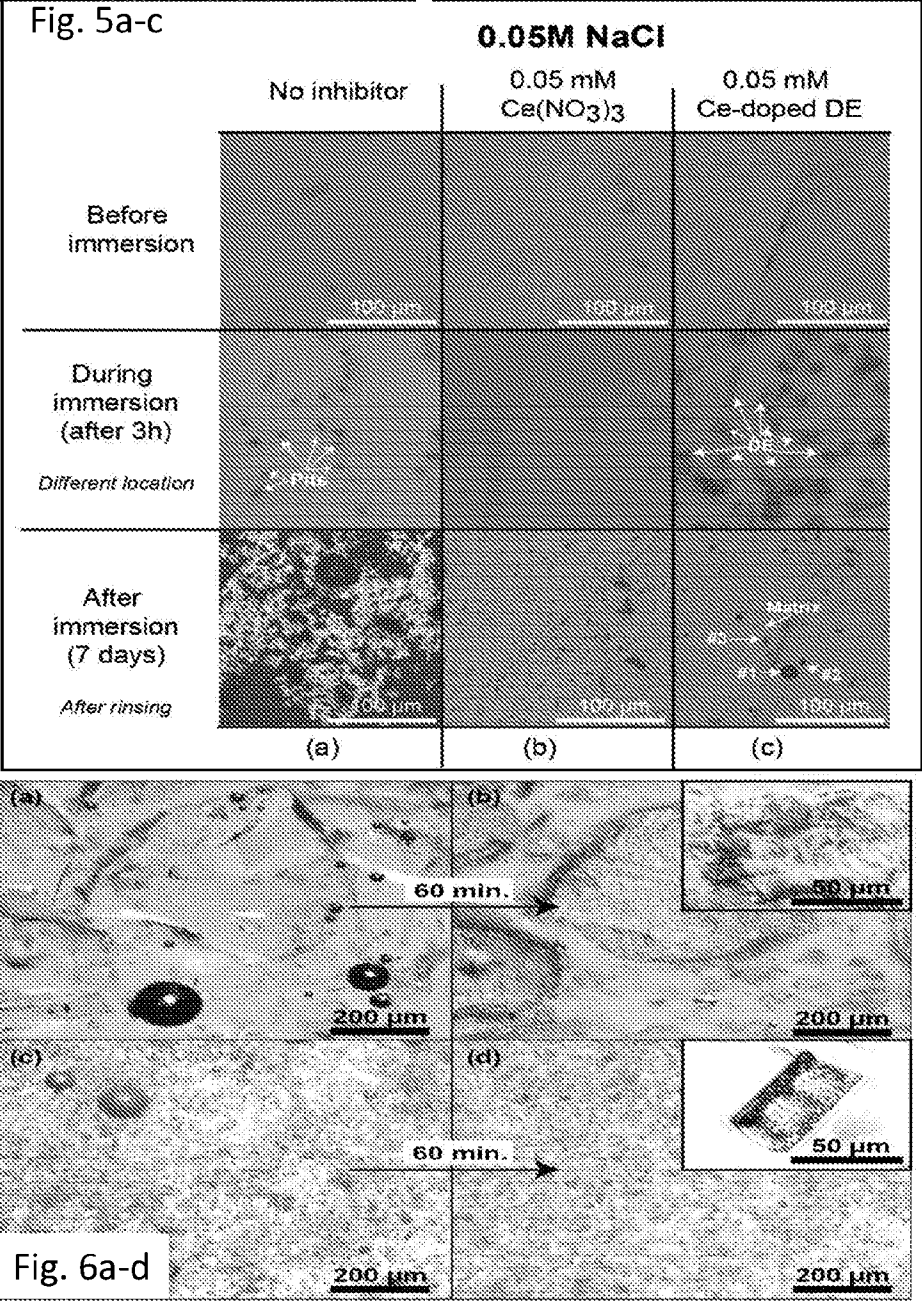
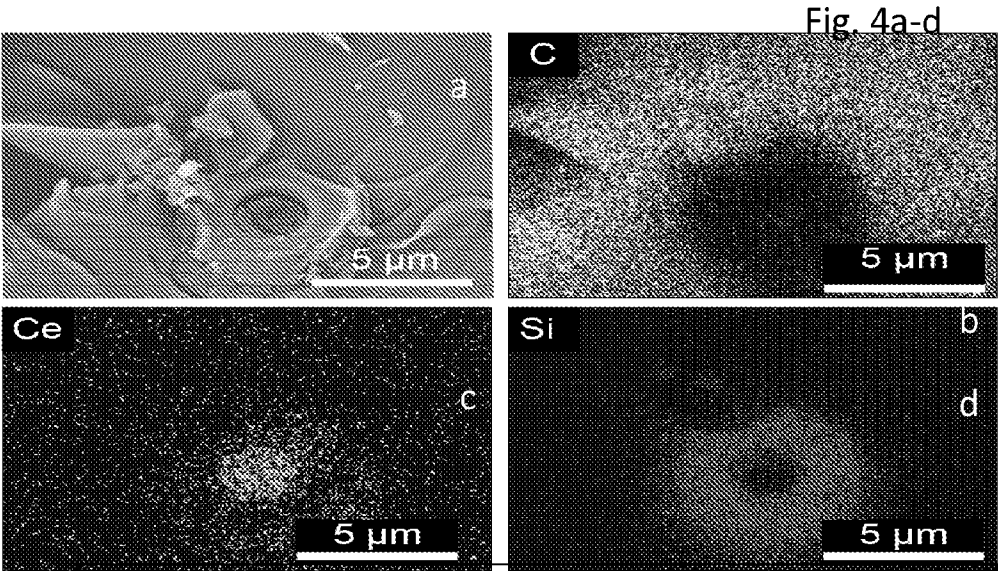


Fig. 3



INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2018/050161

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	C09D5/00 C08K9/10	C09D5/08 C09D5/16 C09D7/62 C08K3/36
ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) C09D C08K		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2010/148158 A1 (ISP INVESTMENTS INC [US]; PREMACHANDRAN RAMAN [US]; NARAYANAN KOLAZI S) 23 December 2010 (2010-12-23) claims 1,4,6,12,14 -----	1-20, 22-27
A	EP 1 024 181 A1 (DAIMLER CHRYSLER AG [DE]) 2 August 2000 (2000-08-02) claims 1,3 paragraphs [0011], [0001], [0004], [0015] -----	1-27
A	AU 2012 101 866 A4 (MACADAMIA OILS OF AUSTRALIA PTY LTD) 31 January 2013 (2013-01-31) page 2, paragraph 5 claims 1-3 -----	1-27
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 16 May 2018		Date of mailing of the international search report 01/06/2018
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Mill, Sibel

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NL2018/050161

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

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

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1-16(partially)
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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

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

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

Remark on Protest

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

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1-16(partially)

The present claims 1-27 relate to an extremely large number of possible products (coatings) comprising 1-20 wt % hollow structures and an organic or inorganic compound adsorbed therein or thereto (claim 1), a product coated with the coating of claims 1-20 (claim 21) and their related methods (claims 25-27). Furthermore claim 22 relate to the modification of a natural carrier by an extremely large number of compounds only characterized by a functional feature.

Support and disclosure are to be found, however, for only a very small proportion of the products claimed (see p. 10-ff, Cerium nitrate as corrosion inhibitor, in an epoxy resin based coating).

In claim 1 however, any kind of organic and inorganic active compound is claimed; the list of active compound includes generic terms such as "self-healing", "precursor of a coating", "anti-bio fouling" etc... which are not limiting or clear, since they relate to a result to be achieved.

Non-compliance with the substantive provisions is such that a meaningful search of the whole claimed subject-matter of the claim could not be carried out. The extent of the search was consequently limited (incomplete search).

The search of claim 1 was restricted to those claimed coatings which appear to be supported and their generalisation: hollow structures of Heterokontophyta species from claim 1 encapsulated by compounds according to claims 7-9 and a film-forming polymer as in claim 14.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/NL2018/050161

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