2nd “MUST” WORKSHOP

Self-healing Coatings: Effectiveness and Implementation

BOOK OF ABSTRACTS

VENUE: 28th June, Hotels von Orange, Noordwijk, Netherlands
Fundamental Understanding of Self-Repair Processes: Aspects of De-Adhesion and Corrosion


ABSTRACT

The design of long-term stable and corrosion resistant polymer/oxide/metal interfaces requires the analysis and understanding of interfacial chemical and electrochemical properties. The evaluation of corrosion resistance and revelation of its mechanisms demands the determination of time dependent properties at the highest possible spatial resolution.

The systems under study are nanocontainer modified corrosion protection coatings. The nanocontainers are filled with corrosion inhibitors and are able to sense external stimulus in form of a mechanical damage, presence of corrosive compounds or corrosion attack and do release the inhibitor for the passivation of corrosion sites.

The scope of this work consists of two parts:
- Fundamental understanding of release mechanisms of nanocontainers and the determination of the progress of the self healing effect.
- Investigation of the system performance under real conditions to correlate the results of fundamental research with the observed overall properties like corrosion resistance and adhesion strength.

By using model systems and applying defined defects in the respective coatings, the release processes can be investigated both in-situ from nanocontainer-based coatings and in-vitro from corresponding containers in aqueous solution at different pH values. Liquid chromatography, confocal microscopy and spectrophotometry are used for the measurement of the release characteristics [1-3]. Moreover, the release processes can be monitored and the inhibiting effects, including local anodic and cathodic current densities, release of the specific metal cations and pH evolution, can be assessed by means of electrochemical techniques with high spatial resolution (Scanning Vibrating Electrode, Scanning Ion-selective Electrode and Scanning Capillary Cell) [4-7]. The products of corrosion processes can be analyzed using Imaging Raman/Fluorescence Spectroscopy and µ-FITR Spectroscopy.

For the evaluation of the overall coating performance, Scanning Kelvin Probe technique is applied to model systems to follow the progress of the corrosion processes and delamination front [8,9]. The systems are also investigated by means of FTIR-Spectroscopy to assess their barrier properties for water uptake.

The presentation will cover results on the structure and release properties of the filled nanocontainers, the preparation of defined defects and the complementary analysis of self-repair mechanisms, using a unique combination of spatially resolved electrochemical and analytical tools. The thereby generated knowledge serves as basis for the design of highly stable interfaces between polymeric films and oxide covered metal substrates as well as for development of new protective coatings with active self-repair functionality.

References

**Improvement of anti-corrosive properties of ORMOSIL coatings with loaded inorganic nanocontainers for protection of AA 2024-T3**

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**ABSTRACT**

Organically modified silicate coatings (ORMOSILs) with nanocontainers TiO$_2$ loaded with 8-hydroxyquinoline, TiO$_2$ loaded with 2-mercaprobenzothiazole, CeMo loaded with 3 aminobenzenesulfonic acid and CeMo loaded with 1H-benzotriazole-4-sulfonic acid were developed onto aluminium alloy 2024-T3 in order to protect the substrate from corrosion. The anti-corrosive properties of the resulting coatings have been evaluated using electrochemical impedance spectroscopy (EIS). We observed a significant improvement of the corrosion protection properties of the films by addition of nanocontainers. The total impedance value is increased by more than one order of magnitude in the case of the coatings with nanocontainers TiO$_2$ loaded with 8-hydroxyquinoline and two orders of magnitude in the case of the coatings with nanocontainers TiO$_2$ loaded with 2-mercaprobenzothiazole and CeMo loaded with 3 aminobenzenesulfonic acid and 1H-benzotriazole-4-sulfonic acid compared to the coatings without nanocontainers. The impedance value at low frequencies for coatings with TiO$_2$ nanocontainers is increased after long exposure time in corrosive environment suggesting possible self healing effect by releasing the inhibiting ions from the nanocontainers. Also, ORMOSIL coatings with nanocontainers have improved barrier properties. The structure properties of the coatings have been analyzed by scanning electron microscopy (SEM) and Raman spectroscopy.
A coating combination of self-healing polymers and corrosion inhibitors for active corrosion protection of metals

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ABSTRACT

A polyurethane (PU) based segmented block copolymer with soft phases was deposited as a coating. This physically crosslinked polymer system shows a self-healing ability based on the fracture and reformation of thermally reversible physical bonds in the polymer matrix. Because heat is necessary to trigger and assist the healing process, these materials are classified as non-autonomic healing polymers. The investigated polymer system is generally not used for coating of metals, hence its potential as a coating material was explored. Additionally cerium nitrate was added to the coating formulation as corrosion inhibitor. As such a multiple action self-healing coating system was created based, on the one hand, on the inhibitor passivating the metal when the coating is damaged and the metal exposed to a corrosive environment, and on the other hand, on the ability of the coating material itself to physically heal a sustained local damage resulting in the repair of the barrier properties. The healing ability of this combined polymer system was studied in bulk and as a coating using various thermomechanical analyses and Electrochemical Impedance Spectroscopy (EIS). It is shown that when the coatings are locally damaged by scratching, a thermal treatment to a temperature above the melting point of the soft phase in the block copolymer and below the melting point of the hard PU phase, results in coating repair as observed using AFM and in a regaining of its barrier properties as observed with EIS. The additional effect of the incorporated inhibitor is also shown using EIS.
ORMOSIL Coatings Containing Loaded Nanocontainers for Corrosion Protection of Stainless Steel

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ABSTRACT

This study focuses on the corrosion protection of stainless steel by applying an Organically Modified Silicate (ORMOSIL) coating that is integrated with conductive polymers (polypyrrole and polyaniline) and contains ceramic nanocontainers loaded with corrosion inhibitors. The effect of the curing time and temperature parameters to the properties of the formed coating were investigated. Moreover, the ability of the loaded nanocontainers to release the inhibitor upon external trigger (e.g. exposure to aggressive environment) in order to provide self-healing of the surface was studied, too. The anti-corrosion properties of the formed coatings were examined electrochemically via electrochemical impedance spectroscopy (EIS); the composition and structure were investigated via RAMAN, Fourier Transform Infrared Spectroscopy (FT-IR) and Energy Dispersive X-Ray Analysis (EDX), and the morphology was determined with Scanning Electron Microscopy (SEM). It is concluded that the curing temperature and time play important role to the structure of the network and therefore to the properties of the coating system as well as the choice of the inhibitor. An increase of three orders of magnitude of the total impedance value is acquired compare to the uncoated substrates when the curing temperature and time are 80 °C and 15 min, respectively.
Multifunctional coatings for cost effective offshore wind energy - NOWITECH -

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ABSTRACT

This poster presents the ongoing R&D activities related to self healing coatings applied to cost effective offshore wind farms within the Norwegian Research Centre for offshore wind technology (NOWITECH). NOWITECH is part of the Centre for Environment-friendly Energy Research (CEER) scheme, which is established to conduct concentrated, focused and long-term research of high international calibre in order to solve specific challenges in the field of energy and the environment. The main objective of this centre is pre-competitive research laying a foundation for industrial value creation and cost-effective offshore wind farms.

Wind as a clean, inexhaustible, indigenous energy resource, is one of the fastest-growing and promising forms of renewable energy in the world. It is estimated that within the EU alone, as much as 1000 billion NOK will be spent on this energy source over the next decade. The potential for offshore wind farms at deeper water is huge provided that operation and maintenance costs can be reduced to a competitive level. This requires the improvement of the current turbine technology and application of new material systems, which can tolerate harsh working conditions and significantly reduce the number of maintenance operations. Compared with onshore wind farms, coatings with improved anti-corrosion and erosion properties, de-icing and self healing properties are required when defining the material systems for the offshore windmill. Thus, development of cost-effective new materials and coatings for enhancing tolerance and life time of offshore wind farms, and new knowledge about how materials respond to the extreme conditions is very essential. Novel anti-corrosion / self healing coating based on nanoparticles and micro/nanocontainers are being developed. Coatings with controlled release of active agents under stimuli such as humidity/pH are promising candidates to an efficient protection of the mill parts against corrosion, and hence, will contribute to significantly reduce the maintenance operations.
Development of materials with self repair functions for high performance protective clothing in the fisheries
- Safe@sea -

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ABSTRACT

This work will present newly started R&D activities related to self repair materials applied in coatings for protective clothing in fishery industries. The work is carried out within the frame of the FP7 project, safe@sea, “Protective clothing for improved safety and performance in the fisheries”. The main objective of Safe@Sea is to develop a new generation of advanced personal protective clothing for the fishing industry that will lead to a significant increase in safety without reducing work performance.

Fishing is a profession linked with high risks. There is a high potential for improved safety in fisheries. The increased safety may stem from improved watertightness of workwear and improved airtightness for buoyancy systems. Development of specialty materials with self repair functions will be integrated in existing coating materials to restore the protective outer layer on garments damaged by daily wear and tear. No textiles with an inherent self repair function are currently commercially available for use in protective coatings. The introduction of self repair technology into clothing applications requires new demands in terms of performance and processability, which will be met by developing the materials specifically for the textile field. Microcapsules with healing agents with fast curing properties will be developed and incorporated to the clothing textiles. When the clothing is subjected to damage, the healing agents will be released and, in turn, will restore the coatings.
Development of flexible LEO resistant PI films for space applications using a self-healing mechanism by surface directed phase separation of block copolymers

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ABSTRACT
Polymeric materials experience accumulated physical damage during use on low Earth orbiting structures. Contributing conditions include radiation, thermal cycling and micrometeoroid impact, coupled with atomic-oxygen (AO) attack resulting in a progressive surface degradation, which may be significant over a 25-year lifetime compared with the 5 to 7 years of exposure typical of today’s orbiting spacecraft and the integrity of structures would be lost before the end of the spacecraft’s intended service lifetime. One option for protection of polymers which are especially sensible to LEO conditions is the introduction of thin (15-100 nm) coatings of transparent, LEO-resistant metal oxides. Though the coatings are efficient in protecting polymers, their application imposes severe constraints since their thermal expansion coefficients differ markedly from those of polymers resulting in cracks developing during thermal cycling and penetration of AO through them to the substrate, leading to undercutting phenomena. A more ambitious option is to use siloxane composites, which are converted to SiO₂ by AO interaction. This surface layer is stable in vacuum and inhibits further oxidation in depth. Siloxanes can therefore be exploited in the first instance as coatings. However, more preferential is the use of covalently bound silicon compounds like siloxanes to provide a good adhesion between the convertible top layer and the structural polymeric material. In this case the naturally lower surface tension of the silicon component, which introduces micro-phase separation in covalently connected polymers, drives it towards the surface.
In the study presented, commercially available amino-terminated polysiloxanes with different molecular weights are used for the synthesis of PI-b-PDMS block copolymers in order to verify in extended testing their performances as LEO resistant polymeric material and to perform a structural optimalisation with respect to maximum protection. A variation of the PDMS block length enables a control of the level of surface enrichment and the block length of the PI controls the gradient of surface composition. The synthesized polymers and casted films show sufficient mechanical and thermal performance (E-modulus 5 - 6 GPa, Tg ~270-280 °C, elongation at break 4-15 % and tensile strength 50-150 MPa). Already for block copolymers with a load of 2% PDMS a complete surface coverage of the PDMS has been found. The transfer of the surface enriched PDMS layer into a thin silica layer results in a decrease in AO erosion rate of the material since the formed silica layer protects the underlying material from oxygen initiated erosion. Such polysiloxane-block-polyimides have a high potential to provide many advantages of a space-use material and can especially improve reliability, design flexibility, and cost effectiveness especially for LEO spacecrafts, especially since they show damage healing of the protective surfaces upon further AO irradiation.
Self-healing coatings for the corrosion protection of magnesium alloys: embedding encapsulated corrosion inhibitors into anodizing layers

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ABSTRACT
The widespread application of magnesium alloys is still considerably hindered by their high susceptibility to corrosion. Coating systems with self-healing properties are a promising approach in dealing with this issue, as they feature sustainable corrosion protection. Since self-healing chromate coatings have been banned in the European Union for their impact on health and environment there is an increased demand for alternative, harmless and comparably protective surface treatments.

The aim of this project is the development of anodizing coatings with selfhealing properties for magnesium alloys. These coatings should be generated at low voltages and in non-toxic electrolyte solutions in order to render the process cost-efficient and environment-friendly. Self-healing properties shall arise from the incorporation of nanocontainers bearing corrosion inhibiting substances into these coatings. In the case of corrosion or physical rupture these substances should be released in the respective areas. One class of corrosion inhibiting substances to be applied are SAM (self-assembling monolayer) monomers, capable of forming hydrophobic films which prevent the intrusion of water and corrosion promoting ions. The second class are inorganic compounds like lanthanide cations, which inhibit corrosion by passivating either anodic or cathodic sites of the corroding substrate.

So far, our results involve comparative electrochemical tests (I/E) concerning the corrosion inhibiting properties of potential corrosion inhibitors. Anodizing of AZ31 was achieved at low voltages with the support of ultrasound. Further tests dealt with the combination of anodizing and the incorporation of SiO2 nanoparticles into the resulting anodizing layer in a one-step synthesis.
Incorporation of nanoparticles and nanocontainers into hard anodizing layers on aluminium for enhanced wear and corrosion protection

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ABSTRACT
Established procedures for wear and corrosion protection of aluminium like plasma-chemical oxidation and classic hard anodizing are known to have one significant disadvantage: the extremely high energy input to reach the required voltages. Additionally extensive technical equipment for cooling of the baths is needed due to high heat evolution. Therefore, increasing demand for procedures providing comparable wear and corrosion protection at a lower energy input exists in industry. The aim of this project is the development of an alternative procedure based on a reference process, the classic hard anodizing. During the anodizing process wear-resistant nanoparticles and inhibitors embedded into nanocontainers should be incorporated simultaneously to reach the demanded wear and corrosion protection already for thinner layers. This means that two processes, the anodizing process and the electrophoretic deposition of the nanoparticles and nanocontainers, should take place under the same conditions. Here we present first results about the surface functionalization of the nanoparticles and nanocontainers chosen for the incorporation into the anodized layers. This functionalization with a negatively charged polyelectrolyte is expedient due to the strong acidic conditions necessary for classic hard anodizing and the required negative surface charge of the particles to deposit on the anode. The influence of voltage, particle size and particle concentration on the particle content in the anodizing layers are investigated. Further, the distribution of the particles in the layer is studied under varying current-voltage regimes.
Synthesis of durable microcapsules for self-healing anticorrosive coatings

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ABSTRACT
Self-healing materials have become a very intense field of research in the last decade. These materials have a built in capability to retain functionalities and restore structural integrity autonomically after material damage, giving advantage of a long service life and costs reductions to the objects they are used for.
In this work a self-healing concept is applied to development of epoxy-based anticorrosive coatings and utilizes incorporation of microcapsules, filled with reactive agents, into the coating matrix. Upon small damages to the coating the reagents are released from the capsules and react forming a cross-linked network which heals the crack. However, to make the concept work, microcapsules have to be strong enough to remain intact during storage, coating formulation, and application. Furthermore, the capsules must remain stable for many years in the dry coating.
Laboratory experiments, primarily conducted on encapsulation of bisphenol-A epoxidised resin into poly(urea-formaldehyde) shells, revealed a number of challenges associated with the synthesis of stable microcapsules. It was found that the nature of the core material strongly affects the microcapsule stability and performance. It also appeared that experimental procedures developed for certain core materials were not suitable for encapsulation of others without modifications. Results of experiments, aiming at finding optimal conditions for robust microcapsules production, will be presented.
ABSTRACT

Occurring due to various mechanisms, cracks in concrete allow water and chemicals to ingress what may enhance the corrosion of embedded steel reinforcement and the deterioration of the concrete structure. An active crack-healing technique based on the incorporation of calcium lactate (as a healing agent) and alkaliphilic spore-forming bacteria (as a catalyst) in the concrete matrix was suggested by H.M.Jonkers. Being in contact with water, bacteria seal the crack through the metabolically mediated calcium carbonate precipitation.
In the present work, the process of bacterial sealing the crack is formalized as a moving boundary problem with Neumann’s conditions. The mathematical model developed with use of several computational algorithms to study this process is described.
A MULTITUDINAL CORROSION INHIBITOR ASSESSMENT ON NINE METALS

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ABSTRACT

The search for non-chromate corrosion inhibitors has been ongoing for many years. Many inhibitor types have been investigated, including inorganic oxyanions, cathodic inhibitors such as the rare earths, sacrificial species such as Mg particles in organic coatings, organics, both neutral and anionic, and multifunctional inhibitors containing both cathodic and anodic inhibitory functionalities. Given the large number of potential inhibitors under investigation, high throughput techniques have been developed in recent years to assist in preliminary identification of promising inhibitors worthy of more comprehensive studies. This paper presents an assessment of over 100 inhibitors tested under 3000 combinations of parameters, including concentration and substrate metal. The assessment was performed by measuring the currents between pairs of the same metal configured into a single mount termed the multielectrode. This allowed for multiplexing between pairs of electrodes so that data for all metals could be obtained in the same experiment. The metals assessed included pure aluminium (99.999 wt %), AA2024-T3, 7075-T6, pure iron (99.95 wt %), stainless steel 316, mild steel (98.44 wt % Fe), pure zinc (99.99 wt %), pure magnesium (99.9 wt %) and AZ31 magnesium alloy. All inhibitors were assessed as a function of concentration from 10^-4 to 10^-2 M in 0.1M NaCl. This assessment was used as an indicator of the critical concentration above which the inhibitor showed sustained inhibition. Several promising candidates were identified, including some aromatic and substituted heterocyclic compounds.
Risk Assessment in Nanotechnology Applications

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ABSTRACT

Nanomaterials offer a promise of evident improvements in a great number of industries. Nevertheless, they initiate new challenges to manage the emerging risks of related field of science. Risks in nanotechnology applications may arise due to non- or poor performance of a system, where the analysis of the risk is performed quantitatively by means of modeling techniques. Besides, risks of adverse/unexpected effects or impacts (e.g. risks of occupational health and safety) and risks over the life-cycle of products and technologies (e.g. unexpected problems in recycling of nanomaterials) are other types of potential risks, which are tackled by qualitative assessment methods.

This paper introduces an example on assessment of the risks in application of nanotechnology to protect the material surfaces against corrosion degradation. The protection is based on providing self-healing features at the place of small defects on material surfaces. Considering a variety of possible scenarios, different aspects of risks are assessed qualitatively by means of collecting data through surveys, as well as experimental results and expert opinions. A consequence-likelihood matrix is used to monitor the level of risks and rank them for further analysis and treatment. Furthermore, quantitative risk assessment is carried out by the use of advanced computer aided simulation techniques. Finally, it is shown that the joint of all these practices will help to establish a comprehensive risk management plan.
Self levelling paper coating layers

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ABSTRACT

The goal of this project is the development of concepts for co-binder systems for the enhancement of self levelling properties of paper coating colours. This self levelling is especially intended to reduce the intensity of application induced coating defects directly after the metering rod.

In general it has been observed in the past, that due to the properties of the binder and especially of the co-binder or thickener the levelling in a coating colour may be influenced. Nearly all modern binder systems contain a synthetic polymer dispersion (latex) as binder. However, before around 1950 natural polymer binders (Casein, Gelatine etc.) were used almost exclusively. In order to call to mind the advantages of Casein regarding levelling properties, we carried out advance tests using a common sheet fed offset coating colour, consisting of only carbonate and no kaolin pigment and of organic binder for which half of the latex was replaced with casein. This colour was then used for coating with a rod metered lab coater. In the course of this, grooves were provoked deliberately using a wound coating bar. As a result a clear difference could be observed – for the casein containing colour the grooves are far less pronounced than for the colour without casein.

In this research project it is planned to increase coating levelling in pigmented coating colours through partial substitution of latex binder with known self levelling binders. The insights regarding the working mechanism shall then be transferred to other co-binder systems.

This research project (duration from March 2010 to February 2012) is being funded by the German Federal Ministry of Economics and Technology BMWi (IGF research program, IGF 15739 N).
Design of Durable Coating Using Self Healing Bitumen

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ABSTRACT

Self healing property of bituminous materials has been known for since 1970s. In addition, bitumen is also regarded as one of the best adhesives in the world with large quantity. Aging and cracking will influence the durability of coatings. So a self healing bitumen-based coating can be designed as a coating to diminish the crack and extend the service life.

Experimental investigations were carried out to understand and quantify the self healing capability of bituminous binders when the binder starts to harden due to aging, or when cracks have initiated and propagated. The results indicate that the soft bitumen itself exhibits excellent self healing capacity, which is mostly relied on the flow-driven process to heal the cracks. In addition, the polymer modification, like Styrene-Butadiene-Styrene also shows positive effects on slowing down the crack propagation in microcrack scale, but indicates retardation of healing process in macrocrack scale.

From the experimental results, a durable coating can be designed using self healing bitumen at three different levels as follows:

Level I: soft bitumen (basic healer) + anti aging agent
Level II: low modulus polymer modified soft bitumen + anti aging agent

Low modulus polymer can be used for providing rapid elastic response for bituminous binders without changing too much flow properties of bitumen, which could improve the healing/recovery of the mechanical property in no crack or microcrack scales. In addition, soft bitumen is also needed to provide enough flow for both low and high crack scales. Hence, self healing over all cracks scales can be expected.

Level III: low modulus self healing polymer modified soft bitumen + anti aging agent

According to Level II, low modulus polymer/rubber could improve the elastic response, and that would also act as filler in high crack scale where the network is already broken. In this case, a kind of low modulus self healing polymer could be useful to provide additional healing from polymer itself, hence to improve the self healing property of high damage scale compared with level II.
A critical comparison of routes towards self healing materials and coatings

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ABSTRACT

Since the introduction of the self healing concept via liquid encapsulation, a range of alternative physical and chemical and even biological routes to realize self healing of surface cracks in coatings and bulk materials have been proposed and initial results have been presented. The routes depend very much on the nature of the material and large differences exist between the approaches for polymeric materials and that for inorganic materials. In this presentation, the various routes and their advantages and drawbacks will be compared. The analysis shows that the liquid encapsulation approach has the highest level of autonomous repair, but has major limitations as far as final property improvement is concerned. In case stimulated self healing (i.e. healing with the temporary addition of additional energy in the form of heat or phonons) is allowed, reversible chemistry routes seem the most attractive. In the case of inorganic coatings, oxidative healing via an expansional oxidation process at elevated temperatures offer the best chances of success. Surprisingly, even multiple healing seems achievable via this route. Finally, some simple mathematical models for the optimization of self healing behaviour will be presented and compared to the insight gained from mathematical models for the complex sequence of healing events in skin healing.
Development and characterization of self-healing anticorrosive organic coatings


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ABSTRACT

A self-healing material has the built-in ability to partially or fully repair damage occurring during its service lifetime. In the field of anticorrosive organic coatings this concept can be applied in three different ways which can be applied separately or combined: recovery of the barrier protection, recovery of the active protection by inhibitor release, and recovery of the adhesion. [1]

The development of self-healing anticorrosive organic coatings is a complex process that combines several approaches. This work shows three of the main lines of research performed by the consortium in this new research area: first, the development of high-throughput techniques for the selection of novel, eco-friendly inhibitor formulations, which includes the development and validation of the so called multielectrode [2] and multichannel [3] high-throughput techniques; secondly, the introduction of the selected inhibitors into organic coatings and the evaluation of their self-healing capabilities [4]; and third the development of self-healing systems for the recovery of the barrier properties of the coating by using a hydrophobic and reactive silyl ester [5].

**Inhibition of Underfilm Corrosion on Aluminium and Zinc surfaces by in-coating Smart Release Pigments**

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**ABSTRACT**

The work presented will focus on the use of both hydrotalcite (HT)-like anion-exchange clays, and naturally occurring cation-exchange bentonites as novel anti-corrosion pigments. Experimental findings on two technologically important metal surfaces will be described. Firstly, in-situ scanning Kelvin probe potentiometry is employed to quantify the inhibition of filiform corrosion (FFC) on AA2024 aluminium alloy substrates by both rare-earth metal exchanged bentonites and HT-based pigments. Although cerium (III) and yttrium (III)-exchanged bentonite pigments are largely ineffective in reducing rates of FFC propagation, in contrast HT-based pigments are shown to be highly effective inhibitors. The efficiency is greatly improved by exchanging the native carbonate ions with anionic species which act as chelating agents for copper ions. When in-coating HT pigments are employed to forestall corrosion-driven cathodic disbondment of a model organic coating on the zinc surface of hot-dip galvanized steel, their efficiency is highly dependent on the nature of the exchangeable anion present, and only work effectively when chromate anions are incorporated within the HT matrix. Bentonite-based pigments are shown to profoundly inhibit cathodic disbondment when exchangeable zinc (II) ions are present and the efficiency is attributed to a reinforcement of the amphoteric surface oxide. The observation of synergistic interactions between certain anion types and group II cations will be also be presented for systems where both in-coating cation and anion exchange pigments are present.
Modelling of multifunctional anticorrosion coatings

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ABSTRACT

In the study three conceptually different approaches to modelling of anticorrosion coatings are considered. According to the discrete model, the simulation runs on a 3D lattice with cubic topology. During a single simulation run lattice gas particles penetrate the interior of the film and eventually reach the bottom of the film. Simultaneously the particles can be absorbed in traps, which have however finite absorption capacity. The traps are placed randomly in some lattice nodes. The total density of the traps does not exceed a few percents. During the simulation two quantities are measured: in each node – real-valued concentration of diffusing particles and in traps – real-valued occupation of the traps related to the amount of trapped particles. The propagation of diffusion front is the phenomenon under study. It is particularly interesting how properties of the coating influence the time of propagation through the coating.

Due to their 3D nature, simulation of a discrete system, although readily incorporating macroscopic features of the coatings, are time consuming, especially for large lattices. To overcome this limitation a set of integral and differential equations is proposed to effectively model the anticorrosive protection of the coatings. The parameters related to the water in-flow and out-flow from and to the surrounding have exactly the same meaning in both models. The correspondence between traps capacity and density and parameters of the effective equations are derived numerically. It is shown that there is excellent agreement between discrete and effective model. The convergence of the numerical results with respect to spatial and time step refinement is also studied.

To better understand the nature of anticorrosive protection of the coatings, the effective equations are solved analytically in the limit of large capacity of the traps. It follows from the analytical solution that there exists a transient equilibrium state, which is an attractor in the time evolution of the water concentration profile. The shape of this attractor profile depends crucially on the diffusion coefficient, the rate of trapping and the rate of water uptake from the surrounding. The duration time of the transient equilibrium is determined by the capacity of the traps. If the available capacity falls down to zero somewhere, the density profiles exits the transient equilibrium and evolves towards global equilibrium linear profile. The above scenario has been confirmed in numerical simulations and excellent agreement between numerical and analytical solution has been observed. The existence of the transient profile explains the results of the laboratory experiments on water uptake and provides a tool for quantifying the quality of anticorrosive action of nano-capsules.
Multi-action corrosion protection by remendable polymer coatings

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ABSTRACT

Due to limitations on the use of chromium conversion coatings by European and international directives, a drive to develop ecologically sound self-healing systems has been initiated. The self-healing capacity of a segmented block-copolymer based on soft poly(ε-caprolactone) (PCL) and hard polyurethane (PU) segments, with a varying ratio of PCL and PU-segments, is examined in this work. This polymer system exhibits non-autonomic self-healing behavior triggered by an increase in temperature. Moreover, to incorporate an autonomic response, a cerium salt based inhibitor was added to the self-healing polymer system. This innovative approach leads to multiple action self-healing coatings.

The macroscopic self-healing properties of the coatings were characterized using Electrochemical Impedance Spectroscopy (EIS) [1]. An increased amount of hard PU segments in the polymer backbone had a negative impact on the thermally induced healing of applied scratches due to a loss of mobility.

The healing of micro-scratches applied using Nanolithography on the surface of the coatings was examined by AFM. Again the observation was made that an increase in the percentage of hard segments acts as a resistance to the self-healing ability of the polymer.

The healing effect of the incorporated cerium based inhibitor was investigated by Scanning Vibrating Electrode Technique (SVET), mapping the anodic and cathodic areas on a surface which are linked to corrosion processes. If the damaged polymer coatings do not contain the cerium inhibitor, clear delamination of the coating was observed after 8 days. Incorporating the cerium inhibitor in the coating resulted in a total inhibition of the corrosion processes.
MODIFICATION OF EPOXY ANTICORROSIVE COATINGS WITH LAYERED SILICATES

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ABSTRACT

Economic impact of corrosion on the industry is a very serious problem. It has been shown that worldwide direct losses due to corrosion exceed $1.8 trillion per year [1]. In particular corrosion is a serious problem in automotive, maritime as well as aerospace industry. Therefore, many methods for protecting metal surfaces have been developed for many years. One of the most commonly used type of anticorrosive coatings are polymer epoxy paints, because of their good barrier properties and excellent chemical resistance. In recent years some epoxy and other polymer microcomposites and nanocomposites with different additives, which improve their properties have been studied [2,3]. Layered silicates are promising materials that might be used for epoxy resin modification, either improving their barrier properties with exfoliated plates or trapping water into clay microparticles. However, the main problem is low compatibility of inorganic silicates with organic matrixes and for this reason clays have to be modified before mixing with polymers. Modification can be performed by treating clays with, among the others, aminosilanes, organoammonium or phosphonium salts [4,5].

In this study we focused on modification of anticorrosive, organic solvent based as well as water based epoxy coatings with laponite clay nanoparticles. Epoxy coatings with different amount of laponite and with laponite modified with Bis-(2-ethylhexyl)phosphate) were prepared. Morphology and barrier properties of resulting composites were investigated by means of infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS).

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References: