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Chapter 7(20): The use of nano/micro-layers, self-healing and slow release coatings to prevent corrosion and biofouling

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Abstract: The mitigation of corrosion and biofouling is a challenge. Through application of chemicals and special techniques can slow these undesired processes, an effective resolution requires a multidisciplinary approach involving scientists, engineers, and metallurgists.

In order to understand the importance of the use of nano- and microlayers as well as self-healing coatings, the basic concepts of corrosion, corrosion mechanisms, corrosion inhibition and the microbiologically influenced corrosion will be summarised.

The preparation, characterization and application of Langmuir-Blodgett and self assembled nanolayers in corrosive and microbial environment will be discussed. Preparation and characterization of microcapsules/ microspheres and their application in coatings will be demonstrated by a number of examples.

Keywords: nano- and microcoating, self-healing, slow-release, anticorrosion, antifouling

7.1 Introduction

Corrosion is a well-known problem all over the world. It consumes a significant part of the gross national product (GDP) of developed and developing countries. A number of authors have provided comprehensive introductions to corrosion mainly in aqueous and wet environments (Jones, 1991; Kaesche, 2003; McCafferty, 2010). Corrosion is the destructive result of the chemical/electrochemical reactions between metals and the environment. Corrosive reactions involve water in either liquid or condensed phases. Most corrosion reactions are electrochemical processes. These involve electron or charge transfer in aqueous solution which leads to metal dissolution (anodic reaction). Depending on the pH of the solution, either hydrogen or hydroxonium ions evolve, resulting in oxides, oxy-hydroxides, hydroxides and salts formed on the metal surface (cathodic reaction). The electrochemical potential or electron activity affects the rate of corrosion reaction. To understand corrosion it is necessary to discuss briefly the types of corrosion and the reactions involved.

Corrosion occurs in various forms.

- *Uniform corrosion:* The metal surface must be compositionally uniform; the aggressive environment has the same access to all parts of the metal. This type of

corrosion is mainly characteristic of atmospheric corrosion and of corrosion in acidic media. Uniform corrosion is predictable.

- *Crevice corrosion*: Crevice corrosion occurs at metal-metal interfaces and is caused by retention of water from the atmosphere when the outer surface is dry. A crevice shields a part of the surface and enhances the formation of differential aeration and ion concentration cells. Both play an important role in the initiation and propagation of the crevice.
- *Pitting corrosion*: this is the result of a localized, rapid penetration of aggressive ions which produce deep or undercut pits. Pitting corrosion often remains undetected until the bulk metal is perforated. The continuous presence of water and chloride ions influences the growth of the pits. In the case of stainless steels, pitting corrosion can occur in neutral-to-acidic solutions in the presence of chloride ions. Iron and aluminium pit in alkaline chloride solutions by mechanisms similar to the stainless alloys but less aggressively. Pitting corrosion is unpredictable. Its rate is variable and depends on the migration of corrosive elements into and out of the pit. The differential aeration cell may be considered a macro model for the initiation of pitting and crevice corrosion (Tsutsumi *et al.*, 2007).
- *Galvanic corrosion*: When two dissimilar metals are connected electrically, a galvanic cell is formed. In a corrosive electrolyte when two dissimilar alloys (having different corrosion potential) are coupled, one corrodes and the other is protected from corrosion. This type of corrosion may be avoided by eliminating the galvanic couple. The metal or alloy, which is less noble, will corrode. Galvanic attack is concentrated in small areas and relative surface area influences the rate of galvanic corrosion. A larger cathodic area provides a greater surface for the reduction reaction, and the anodic dissolution rate must increase to compensate.

Other types of the corrosion are (Song, F.M., 2009; Sanchez *et al.*, 2007; Stack, M.M. *et al.*, 1999):

- stress corrosion
- hydrogen damage
- intergranular corrosion
- environmentally induced cracking
- dealloying
- erosion corrosion

7.2 Corrosion of different metals: mechanisms, monitoring and corrosion inhibitors

Scully and Marcus (Scully, 1983; Marcus, 2005, 2011) have contributed to the understanding of corrosion considering the electrochemical, chemical and adsorption processes on different types of metal deterioration.

Corrosion processes are strongly influenced by environmental perturbations at the surface. Important classes of variables that impact the type of corrosion include the nature of the electrolyte (conductivity), dissolved chemicals (inorganic/ organic solids and gases e.g. oxygen, carbon dioxide), pH, temperature and the suspended components in the electrolyte.

Corrosion in aqueous environments proceeds via an electrochemical mechanism, when coupled anodic and cathodic reactions take place at unique sites on the metal/environment interface. One part of the surface (anode) is exposed to electrolyte and the metal dissolves.

The other surface, where reduction but not metal dissolution takes place is the cathode. For a corroding metal (M) the general formula of the anodic reaction consists of a number of reaction steps:

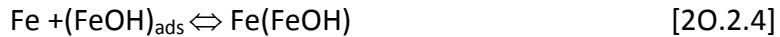


In the case of iron, the reactions in an aqueous environment are as follows:



One explanation for the anodic processes is that the water molecules are first adsorbed onto the metal surface altering the adsorbed products.

When the reaction is of a catalyzed type:



Then in this case, the second reaction determines the rate of metal dissolution. The final step in both mechanisms is the transformation of the $[Fe(OH)]^+$ species:

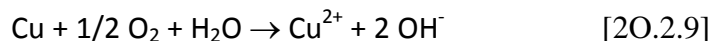


The rust layer formed on the anode contains different iron oxides, as well as hydroxides which are porous and penetrable by aggressive ions and gases. Aerobic corrosion initially accelerates the metal dissolution in the pores (Sherar *et al.*, 2011).

Another example is copper. The dissolution proceeds in two steps (Crundwel, 1992):



When oxygen is present in the neutral aqueous solution, the anodic dissolution of copper proceeds as follows:



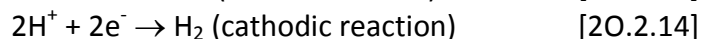
The presence of ions such as Cl^- that can form complexes with the copper ion in aqueous solution results in the formation of $CuCl_2$. In a near neutral solution, saturated by oxygen, the following reactions occur:



In a third example, when the environment is acidic and the metal is zinc dipped in hydrochloric acid, the following overall reaction represents dissolution:



This can be broken down as follows:



In neutral/alkaline aqueous solution, oxygen reduction represents the cathodic reaction.

In the absence of other reduction reactions, water will be reduced and the end products of the cathodic reactions (H_2 , H_2O or OH^-) will then depend on the pH of the solution.

Corrosion in aqueous solution involves electron or charge transfer. A change in electrochemical potential or electron activity at the metal surface has a profound effect on the rate of corrosion. When a metal is submerged in solution, mobile electrons on the metal surface form a complex interface and water molecules of dipole character will face the metal with the oxygen atom. An oriented solvent layer is formed on the metal surface which inhibits the close approach of charged species from the bulk solution. Charged ions attract polar water molecules which further insulates them from the conducting surface. The result

is an electric double layer (referred to as the outer Helmholtz plane) which regulates charge transfer as well as limiting electrochemical reactions at the surface. During corrosion, aggressive ions or gas molecules penetrate into this double layer, reaching the metal surface and initiating metal dissolution.

In an electrolyte, the rate of corrosion depends on the concentration of ions present, on pH and on temperature. With increasing concentration of aggressive ions, the corrosion rate increases up to a point. When corrosion products cover the metal surface, they can act as a screen and thereby decrease migration of further undesired corrosive components to the solid surface. However, this layer is not homogeneous but porous and allows further penetration of aggressive molecules to the metal surface.

Corrosion also depends on other factors such as the chemical nature of the metal, the microstructure resulting from the manufacture method, heat treatment, and roughness (Malayoglu *et al.*, 2005; Córdoba-Torres *et al.*, 2002). The flow velocity of the electrolyte around the electrodes could further influence the corrosion potential due to disturbed mass transport (Kear *et al.*, 2007).

Pourbaix diagrams thermodynamically predict whether certain reactions will occur on metals covered by aqueous electrolytes. The acidity or alkalinity can influence the metal dissolution/corrosion. Certain metals have a sensitivity to corrosion which depends on pH. pH could also play a crucial role in the degradation rate of mechanical properties, for example in the case of aluminium alloys (Berkeley *et al.*, 1998).

7.2.1 Monitoring of corrosion

There are several techniques that are useful to follow reaction steps and identify interim products, as well as to obtain information on the corrosion mechanisms. Marcus and Mansfeld (Marcus *et al.*, 2005) summarized the major surface analytical techniques, their principles, instrumentation. This book discusses possible application of scanning electron spectroscopy, ion analytical methods, nanoprobe, infrared spectroscopy, Raman spectroscopy, glow discharge optical emission spectroscopy and recent developments in the application of radiotracer methods, nanoscratching, and nanoindentation.

Photoelectron-spectroscopy, Auger-, Mössbauer- and Raman spectroscopy as well as mass spectrometry, electrogravimetry, polarization techniques, electrode impedance spectroscopy (Collazo *et al.*, 2010) all contribute to the understanding of corrosion processes. Salt spray tests yield important information on pitting, intergranular and general corrosion. Mechanisms may also be quantified by optical microscopy and laser profilometry (Kelly *et al.*, 2002; Walton *et al.*, 2012). Electrochemical noise measurement supplies statistical parameters (electrochemical noise resistance, coefficient of variation of current and localization index) and parameters derived from shot noise are related to the type and rate of corrosion (Sanchez-Amaya *et al.*, 2005).

7.2.2 The use of corrosion inhibitors

Corrosion inhibitors are chemicals that can significantly decrease the corrosion rate at very low concentration and where their concentration does not change. The classification of inhibitors depends on their chemical nature (organic/inorganic), on the type of reaction they influence (oxidants, non-oxidants, complex or precipitate former, anodic, cathodic) or on the layer the inhibitors form on the metal surface. There are 2D- and 3D-type inhibitors. The 2D-types hinder the surface reaction by direct adsorption when a neutral monomolecular layer is formed or where adsorption takes place only on the active sites. The 3D-type inhibitors change the activity at the metal/solution interface such that chemicals of low solubility form a protective layer (Mansfeld, 1985; Lorenz, 1986; Kuznetsov, 1996).

In an aqueous environment chromium(VI) salt was a very active inhibitor but since 2005 its use is banned due to its toxicity. Later phosphoric and phosphonic acid derivatives combined with other heteroatoms (sulphur, nitrogen) replaced the chromium(VI). There are

several non-toxic inhibitors that can now replace molecules containing nitrogen, sulphur and phosphorous atoms or aromatic rings (Rocca *et al.*, 2001).

Examples summarized in Figure 20.2.2 a-g show the synergistic effect of some additives that increase the efficacy of an inhibitor (Telegdi *et al.*, 2006). Under neutral conditions, phosphonic acid forms a complex layer on the metal surface that controls the corrosion of mild steel. The presence of divalent cations changes not only the efficiency but the type of inhibition. AFM images show the significant changes to the metal surface. The presence of barium ions results in a continuous film, and zinc ions form small particles precipitated on the metal/solvent interface. The third example with strontium ions is interesting. During the first hour the efficacy increases but later the whole surface is perforated.

The inhibitor layer formation is the consequence of the equilibrium between the sorption-desorption of the inhibitor molecules. The result is physisorption or chemisorptions. The efficiency of the inhibitor molecules depends on the number of the active sites on the metal surface and on their structure. According to Thomas (Thomas, 1976) the inhibitors can diminish the dissolution of the passive layer, can re-passivate the surface with non-soluble chemicals or can stop the pores.

Solvation and complex formation also play an important role in inhibition. The type of molecules used for corrosion inhibition depends on the type of metal, on the environment and on the type of corrosion. The inhibitor efficiency could differ for different metals.

On a galvanic electrode, the influence of alkane carboxylic acids with long alkyl chains and their salts used as inhibitors were investigated using a number of differing techniques. The protective layers formed on carbon steel and stainless steel surfaces, characterized by infrared spectroscopy and atomic force microscopy, showed that the layer formed on the carbon steel was more compact than on the stainless steel (Ai *et al.*, 2006).

Temperature also influences inhibitor efficiency. An example is the octadeceneamide derivative that, following the Frumkin isotherm, forms a protective porous bi-layer. The type of adsorption changes with an increase in temperature and inhibitor concentration (Desimone *et al.*, 2011).

7.3 Microbiologically influenced corrosion (MIC) and biofouling: mechanisms, monitoring and control

MIC was first reported by Garrett (Garrett, 1891) where he discussed the deterioration of lead covered cables by metabolites of bacteria. Later Gaines (Gaines, 1910) explained the high sulfur content in corrosion products with microorganism activity. More detailed investigations on MIC began in 1923 and continued into the forties. The importance of the MIC was accepted and became a subject of mainstream research from 1960.

Microbiologically influenced corrosion is a special type of corrosion caused or promoted by microorganisms with their exopolymeric substances and aggressive metabolites that may render the environment corrosive and increase the rate of material deterioration. An understanding of MIC requires an interdisciplinary approach including chemistry, biochemistry, microbiology and metallurgy. This type of corrosion occurs for example in industrial cooling systems, drinking water and sewage systems, the food industry, during sailing or oil production.

The following summarize the most important phenomena caused by microorganisms (Borenstein, 1994; Kearns, 1994; Videla, 1996; Little *et al.*, 2007; Javaherdashti, 2008). MIC occurs both on metallic and non-metallic surfaces, in the presence or absence of oxygen. The most

dangerous microorganisms are the anaerobic sulfate reducing species (*Desulfovibrio*, *Desulfomonas*); they produce hydrogen sulfide (that causes sulfide stress cracking). In the presence of oxygen, aerobic microorganisms can directly oxidize the sulfur producing sulfuric acid, or can oxidize the iron (including *Thiobacillus thiooxidans*, *Thiobacillus ferrooxidans*, *Sphaerotilus*, *Pseudomonas*, and *Gallionella*).

Microorganisms involved in MIC include bacteria, algae, fungi, plants, and animals. They are less dangerous in planctonic form than in sessile. The accumulation of microorganisms and macroorganisms on wetted surfaces, known as biofouling, is a widespread problem both in fresh and seawater. Biofilm formation consists of a sequence of steps, beginning with adsorption of macro- and small organic molecules at the surface. This conditioning layer is where the organisms adhere and start to build the biofilm. There are many factors that influence film formation (microorganism type, surface roughness, dissolved chemicals, hydrodynamics and diffusive transport) (Lewandowski, 1998; Beyenak *et al.*, 2002).

The biofilm consists mainly of water (75-90%) and of microorganisms, of exopolymers as well as organic and inorganic materials. Forces in biofilms that determine the structure are weak interactions including van der Waals forces, electrostatic interactions, and hydrogen bonds. The anaerobic microbes are close to the solid surface, the aerobic ones near to the water/air interface. The microorganisms with their presence and aggressive metabolites initiate pitting corrosion which begins beneath the biofilm where a concentration of cells forms, leading to localized corrosion.

7.3.1 Monitoring of MIC

There are numerous monitoring techniques which allow evaluation of the impact of microbes on corrosion. If electrochemical methods are applied separately (eg. redox potential, open circuit potential, electrochemical noise analysis, microsensors, scanning vibrating electrode technique, duel cell technique, electrochemical impedance spectroscopy (Little *et al.*, 2007)) it is necessary to use a number of complementary measurements. Change in the redox potential is not selective so that noise analysis is recommended in the case of local corrosion and electrochemical impedance spectroscopy is applicable to general corrosion. Microbiological techniques are useful for the identification of microbes. Spectrophotometric and conductivity measurements are used for quantitative analysis and different staining procedures make visible some constituents of the cell structure.

7.3.2 Control of MIC

MIC can be treated in four ways:

- physical-mechanical treatment (pigging, ultrasound- ultrasonic)
- electrochemical (cathodic protection)
- biological (one bacterium used against another one)
- chemical treatment with biocides (oxidizing, non-oxidizing, chelat former, electrophiles and membrane active)

Chemicals can either regulate the growth of microorganisms or influence the microbial attachment. They must have a broad spectrum as they should regulate both aerobic and anaerobic microorganisms. Coatings of different origin (coal tar, asphaltic bitumen, zinc-aluminum, lead, and plastic) are very vulnerable to MIC. If microbial adhesion and biofilm formation is inhibited, the corrosive impact of micro- and macroorganisms, the rate of pitting, stress and general corrosion will all decrease.

7.4 Inhibition of biofilm formation by nanolayers

Corrosive deterioration could also be decreased by layers. The dissolution of metals in an aggressive environment could be decreased by surface pre-treatment, by application of coatings that could be metallic, non-metallic and organic, and in macroscopic or microscopic layers. These films hinder the direct contact between the aggressive medium and the metal surface, and alter the characteristics (e.g. hydrophobicity/hydrophilicity) to be unfavourable to the aggressive environment. The application of these techniques dramatically reduces the mass of chemicals used as dissolved inhibitors. With special coatings the deterioration processes may be significantly decreased.

As compared to the traditional concept of inhibitors, where the metal is in direct contact with a dilute solution of the active species, nanolayers of anti-corrosive molecules form pre-fabricated protective coatings. The word 'nano' refers to the thickness of such layers, but can also mean that the respective coating contains nanoparticles. In single or multi-molecular layers the oriented molecules are sensitive to pressure, temperature and also to the presence of other ions. The advantages of such nanolayers are that the active molecules are used in smaller quantity, costs are lower and potential environmental impact is reduced.

In corrosive environments these layers can function as anodic, cathodic, and mixed inhibitors, as well as functioning as barrier layers. The same layers could be effective against microbially influenced corrosion by decreasing the surface free energy, hampering the adsorption of the biomolecules and cells (Baier, 2006, Telegdi, 2009, Románszki *et al.*, 2012, Románszki *et al.*, 2012, Románszki *et al.*, *in press*). In addition, the compounds in nanolayers could be toxic for many different microorganisms such as bacteria, (Sun, 2002, 2003; Skrivanova, 2006; Shin, 2007), viruses (Bergsson, 2001) and fungi (Avis, 2001; Wang, 2002), because they interfere with the cell membrane and compromise its integrity, leading to cell death (Fig 2O.4.1a).

In the following sections, Langmuir–Blodgett (LB) films and self-assembled molecular layers (SAMs) will be discussed as they are the most important and best studied nanolayers. SAM layers are of higher industrial importance, while LB films, due to the nature of the process, are of greater scientific interest.

A common feature of SAM and LB films is that they are built up by amphiphilic organic molecules, surface-active compounds and surfactants. In the structure of such molecules, the small hydrophilic functional (head) group and big hydrophobic part can be distinguished. The head group is polar or ionic (carboxylic, phosphonic, sulphonic, hydroxamic, etc.) and is therefore capable of forming strong, often salt-like, ionic bonds with the metal surface, which is crucial for the layer stability. The hydrophobic part is usually an alkyl chain. The tails of neighbouring molecules interact via dispersive forces and also contribute to the stability of the layer. Some amphiphilic compounds used in LB or SAM preparation are presented in Fig.2O.4.1b.

The major difference between LB and SAM films is that the former are the result of a non-equilibrium process, while the latter are formed under equilibrium conditions. Self-assembly occurs spontaneously upon dipping the solid substrate into a solution of the surfactant molecules. Molecules at the air/water interface are forced to build a tightly packed monomolecular layer by compression in the LB-film balance.

Despite their reduced thickness, nanolayers can be studied, measured, and even optically visualized. Techniques and devices include: isotherm recording, static and dynamic contact

angle measurement, Brewster angle microscope (BAM), atomic force microscope (AFM), reflection-adsorption infrared spectroscopy (RAIRS), sum-frequency generation spectroscopy (SFG), X-ray photoelectron spectroscopy (XPS). Since the fabrication of such layers requires a solid, most often metal, substrate, layer fabrication aspects which relate to the substrate characteristics (roughness, cleanness, oxide layer) will also be discussed.

7.4.1 Preparation of Langmuir–Blodgett films

A monomolecular layer with a compact structure at the air/water interface is called a Langmuir film. Such films have been known for several centuries, although it was Irving Langmuir who conducted the first thorough study of them (Langmuir, 1917). Preparation starts by spreading droplets of a dilute solution of an active amphiphilic compound dissolved in a volatile, water immiscible solvent onto a clean water surface (subphase) in the trough of the Langmuir–Blodgett film balance. After evaporation of the solvent, a barrier compresses the molecules until they reach a densely packed state. The stages of compression are recorded, and the change of surface tension (known as surface pressure) is measured and plotted as a function of the area per molecule. Since these curves are usually recorded at constant temperature, for historical reasons they are known as ‘isotherms’ of a Langmuir film (but should not be confused with a Langmuir adsorption isotherm). During compression, the available area for the molecules decreases and the surface pressure increases first slowly, during which time the molecules are said to be in a two-dimensional gas-like state. The surface pressure then starts to rise suddenly with a moderate slope. In this region the molecules are referred to as existing in a liquid-like state. Finally, the slope of the curve becomes even steeper and reaches its maximum value. In this region the molecules are highly packed and ordered, just as in a pseudo-solid state. Any further compression of the film results in collapse. The shape of the isotherm and the location of the Π_c collapse surface pressure, A_c molecular area at collapse and A_0 molecular area in the solid state extrapolated to zero pressure are characteristic of the surfactant type and depend on concentration, temperature, pH and on the ions present in the subphase. Fig.

20.4.2 shows a typical isotherm and the state of the Langmuir film corresponding to each region of the curve. Table 20.4.1. presents the temperature dependent molecular area values in the case of two hydroxamic acids (Románszki *et al.*, 2007).

Dissolved molecules in the subphase may also have an impact on the Langmuir film. For example, bivalent cations are known to contract, stiffen and stabilise the monolayers by forming salt-like or coordinative bridges on metal surfaces (Table 20.4.2.). In the case of metal samples with an oxide layer, the influence of cations on the layer characteristics depends on the valence and the volume of the ions (Wang *et al.*, 2012).

A Langmuir–Blodgett film consists of one or more Langmuir monolayers transferred onto a solid substrate via a perpendicular dipping technique (Blodgett, 1934, 1935). The transfer of the monolayer is carried out at constant surface pressure, and in the high surface pressure region, where the packing order of the molecules is greatest. This high degree of order will be preserved in the LB film on the solid substrate, which accounts for its performance as a protective layer. The substrate is dipped in and pulled out through the interface, and depending on its hydrophilic/hydrophobic nature, high quality multilayers are formed on the solid.

The morphology and properties of the fabricated LB film strongly depend on the conditions of preparation. Langmuir films of some compounds are more sensitive to temperature than others (Románszki, 2008; Telegdi, 2005a). The pH of the subphase is also important since it

determines the dissociation state of the head groups, and hence the bonding to the metal surface and the structure of the film (Telegdi, 2005a, Telegdi *et al.*, 2006).

Another relevant parameter is the detail of the molecular structure of the film forming compound. The functional group determines the tilt angle of the hydrophobic tails and thus affects the packing of the molecules. Double bonds and bulky substituents present in the carbon chain generally hinder the packing resulting in a more fluid-like behaviour of the film. Chain lengths shorter than 12-14 methylene units are too small to form stable Langmuir and LB films.

7.4.2 Preparation of self-assembled molecular layers

In contrast to the LB films, SAM layers are formed spontaneously upon dipping the substrate into a solution of the film-forming compound and do not require any special equipment. The first reported SAMs were thiols on gold (Nuzzo, 1983). Countless combinations of surfaces and functional groups have been reported.

In conventional systems, the active species adsorb from the solvent by forming SAM layers. As compared to LB films, SAMs are formed in equilibrium systems. The substrate can be of any shape or size but the formation time of the SAM layer may be affected by these parameters.

7.4.3 Study and characterization of nanolayers

Monitoring the contact angle (CA) is possibly the simplest measurement and yields information about how successful the coating procedure has been. The principle was formulated by Young (Young, 1805). There are many different techniques for measuring CAs, but the most common are the sessile drop and the Wilhelmy plate (dynamic) techniques.

In the first approach, a droplet is placed on the surface to be characterized, an image of which is captured by a CCD camera and the angle of contact formed at the gas/liquid/solid interfaces are evaluated. This method can be used in both static and dynamic mode.

Separate measurement of advancing and receding CAs is important for correct surface characterization. The difference between these two values is the CA hysteresis.

The principles of the Wilhelmy plate technique are also well established (Wilhelmy, 1863). The substrate to be studied is perpendicularly immersed in and then withdrawn from the test liquid at a known rate. One advantage of this method is that several immersion cycles can be recorded over a relatively large area, thus the *in situ* changes due to breakage or reorganization of the layer can be studied over time. Surface roughness also affects the measured CA.

Surfaces are often composed of high and low energy domains. An example would be a metal oxide with a loosely packed SAM. In this case, the metal oxide mainly contributes to the receding CA whilst the SAM contributes to the advancing CA. Cassie–Baxter theory (Cassie, 1944) describes the overall CA of such composite surfaces. The measured data allow the calculation of the surface free energy values using Neumann's (disputed) equations of state (Neumann, 1974). Zisman's method can also be used (Zisman, 1963) in which the surface is characterised by its critical surface tension.

SFS is an efficient technique for obtaining information about the molecular level order of the prepared nanofilm, which is directly correlated with its performance as a protective layer (Keszthelyi, 2006). SFS is based on the nonlinear optical phenomenon which occurs when a light beam with a fixed wavelength in the visible part of the spectrum interacts with one at infrared wavelength which scans the surface. The resulting outgoing light beam has a frequency which is the sum of the two incoming ones. This phenomenon is extremely surface sensitive and in a nanolayer, methylene groups in the alkyl chains extended in an all-*trans* conformation do not contribute to the sum frequency generation, they are not 'visible', unless their symmetry is broken in the form of *gauche* defects. On the contrary, terminating methyl groups make a strong contribution to the generation of the outgoing signal. CH₃ peaks present in the spectra indicate a highly ordered, compact film structure with molecules in fully extended all-*trans* conformation. The appearance of CH₂ modes indicates *gauche* defects (Lambert, 2005).

Fig. 20.4.3. compares the spectra of SAM layers of a saturated and an unsaturated compound. Palmitic acid (PA) molecules pack tightly and give rise to strong characteristic CH₃ SFS peaks, while the double bond present in the oleic acid (OA) alkenyl chain causes distorted conformations, resulting in less intense CH₃ peaks and the appearance of CH₂ modes (Románszki, 2008).

7.5 Efficiency of different types of nanolayer against corrosion

In this section results of the application of LB, SAM and other types of nanolayers to metals (iron, steels, copper, and other industrially important metals and alloys) in a corrosive environment are summarized. Types discussed are:

- Alkyl amines
- Alkyl alcohols
- Thiols
- Phosphates
- Sulfates
- Thiosulfates
- Carboxylic acid
- Hydroxamic acids
- Amino acids
- Phosphonic acids
- Sulfonic acid
- Silane derivatives

7.5.1 Alkyl amines and alcohols

Alkyl amines (C10-C18) can form SAMs on SS 316L stainless steel surfaces. As confirmed by XPS, the amino groups are bound to the oxide-free surface of the steel; however the nature of the binding is not clear. According to (Feng, 2007b) these amines cannot control acidic corrosion as they do not form a real SAM layer.

On the other hand, mixed films of C14-amine and C12-thiol prepared by consecutive immersions, show higher inhibition efficiencies though the reason for this is unclear. The use of alcohol nanolayers is not widespread. Octadecanol cannot form a SAM layer on an oxide-free surface of stainless steel 306L (Ruan, 2002).

7.5.2 Thiols

Historically, alkane thiol molecules in SAMs were applied to copper and silver. The thiol group is always bound to the pure metal surface, never to the oxidized surface. SAMs of octanethiol, dodecanethiol, hexadecanethiol, octadecanethiol and docosanethiol protect copper from corrosion in oxygen (Laibinis, 1992 and Jennings, 1996).

Studying the corrosion of copper by XPS revealed that the SAM films of C16-SH and C22-SH protect the metal from corrosion, but the molecules with longer carbon chain in the SAM film offer better protection. Generally, the protective effect is attributed to the densely packed alkyl chains that prevent the penetration of water molecules to the metal surface. The structural changes of the thiol films occurring during the corrosion tests were followed by contact angle measurements in hexadecane. After two weeks SAM films of C8-SH, C12-SH and C16-SH became completely wettable for the hexadecane. When SAM films of 22-hydroxy-docosanethiol (HO-C22-SH) were treated with octadecyltrichlorosilane, an alkenyl chain with 22+18 methylene groups formed a double layer and this was somewhat more effective than that of the simple C22-SH SAM film.

Thiol derivatives of trimethoxysilane (MPTMS) applied at optimal concentration in SAM film preparation efficiently inhibit the corrosion of copper in 100 mM KCl solution (Tremont, 2000; Sinapi, 2004). The highest inhibitor efficiency was obtained in the case of a 30 min SAM formation time. Based on polarization measurements, in the presence of dissolved oxygen the silane films behave as mixed-type inhibitors. Using the grazing angle polarized FTIR technique the presence of a polymer was detected in the adsorbed layer, moreover, from the absence of a S-H signal, it was concluded that the silane compound is bound to the metal by a chemical copper-sulphur bond.

12-(*N*-pyrrolyl)-*n*-dodecanethiol SAM films formed from a 10 mM ethanol solution on polycrystalline copper efficiently protect the metal from corrosion, as shown by polarization and CV studies (Mekhalif, 2001). The main conclusion was that the thiol molecules attach to the copper surface by S-Cu chemical bonds when metal oxide is not present in significant amount. The protective effect of the thiol coating against corrosion was demonstrated also by XPS. Other studies on various alkanethiols (Yamamoto, 1993), octadecanethiol (Zhang, 2005; Hutt, 2005), dodecanethiol (Tan, 2004; Metikoš-Huković, 2007) are also available.

Other studies compare nanolayers of octadecanethiol, 1-dodecanethiol and 1-hexanethiol (Ma, 2003), 1-decanethiol and thiophenol (Whelan, 2003). There is a comprehensive study on hexane-, octane-, decane-, dodecane-, tetradecane- and octadecanethiol SAMs (Ishibashi, 1996), another on decanethiol, dodecanethiol, hexadecanethiol, octadecanethiol (Ruan, 2002) and on thiophenol and its derivatives (Tan, 2006). The conclusion is that the alkyl thiols form a stable nanolayer on oxide-free copper surfaces and that anticorrosion efficiency increases with increasing alkyl chain length.

7.5.3 Phosphates

The advantage of phytic acid is that it is a naturally occurring substance found in vegetable seeds and bran. Its six phosphoric groups make it especially suitable for complex formation with metals. Hao *et al.* produced phytic acid coatings on CuNi 70/30 samples by simple

immersion (Hao, 2008). In 3% NaCl solution EIS and photoelectrochemical measurements were performed on the samples in order to test the anticorrosion efficiency of the formed SAM layers. The morphology of the layers formed was investigated by SEM, and their composition by EDS. It was found that a phytic acid layer is formed relatively easily on a CuNi 70/30 alloy surface. The inhibition efficiency was correlated with the phytic acid concentration and immersion time. Samples prepared by immersion on timescales between 1–8 h exhibited 73–91% inhibitor efficiency.

7.5.4 Sulphates and thiosulphates

There is little published in the literature on sulphate nanolayers. One good example is a study on sodium dodecyl-sulfate and ammonium dodecyl-sulfate (Hong, 2005). Some authors (Lusk, 2001) suggest that SAM films of sodium *S*-alkyl thiosulfate ($R-S-SO_3^-Na^+$) and molecules with various carbon chain lengths (8, 10, 12, and 14) might be potential alternatives to the traditional thiol-based SAMs as protective layers against the corrosion of copper. As the authors correctly point out, the main advantage of such thiosulfates, in contrast to thiols, is that they are water-soluble and more easily applied in industry. The results of EIS, IR, contact angle and XPS measurements indicate that short-chained compounds give lower quality films and thus provide only modest corrosion protection, while SAM films of longer chain compounds are more compact and protect the metal better. However, thiosulfate SAMs are generally less packed, less ordered, and less crystal-like than the corresponding thiol SAMs and thus provide lower protection.

7.5.5 Carboxylic acid

Other types of amphiphiles that can form self-assembled molecular layer on metal surfaces are the alkyl carboxylic acids. In corrosive environments, stearic acid nanolayers were deposited and their inhibiting efficiency investigated (Románszki, 2008; Raman, 2010). Other studies include palmitic acid on aluminum (Tao, 1996), sodium oleate (Li, 2006) and 12-amino lauric acid (Ghareba, 2010) which also demonstrated the usefulness of these layers in mitigation of corrosion.

Studies have shown that longer alkyl chains offer better protection, and the influence of ω -substituents has also been investigated (Raman, 2007; Sahoo, 2009). One study investigated the efficacy of sodium salts of lauric-, myristic-, palmitic-, stearic and 16-hydroxy palmitic acid on passivated iron (Aramaki, 2004). The anticorrosion efficiency increased with increasing hydrophobic molecular part, but the presence of a substituent in the alkyl chain disturbed the formation of a compact nanolayer which leads to decreased anticorrosion efficiency.

7.5.6 LB and SAM films of hydroxamic acids

Fatty hydroxamic acids are another class of potential candidates in corrosion protection. The importance of the SAM layer deposition time for these acids is presented in Figs 20.5.6.1 and 20.5.6.2. With increasing deposition time, the ordering of layers (according to the IRRA spectra) as well as the anticorrosion efficiency (as proven by polarization resistance values obtained from EIS measurements) increases (Fig. 20.5.6.2, Table 20.5.6.1). These nanolayers are more efficient in prevention of pitting corrosion of copper than fatty carboxylic acids (Románszki, 2008).

Fig 2O.5.6 a-b demonstrates how a self assembled molecular layer can inhibit pitting corrosion. The copper surface held in NaCl solution for 20 minutes is full of pits, but the pre-coated surface is still smooth after 60 hours. As confirmed by CA, SFS and also AFM studies, high quality, closely packed, well ordered protective LB films are formed if the chain length is suitably long (16-18 carbon atoms), and when the temperature is kept relatively low (around 20°C). The quality of these LB films is better than those of the corresponding SAM films. According to the results of polarization experiments run with copper samples coated with such SAM and LB films, the corrosion inhibition efficiency is up to 85%, higher in the case of the SAM layers and improves with increasing chain length (Table 2O.5.6.2-3) (Telegdi, 2005a).

XPS and SFS studies revealed that octadecanoyl hydroxamic acid LB layers are compact and well ordered, adopting a predominantly all-*trans* conformation, irrespective of the substrate. On a copper surface, the amount of hydroxide species present decreased after surface modification, indicating that metal hydroxide is necessary for fixing the organic molecules. It is probable that water is desorbed during the measurement (Keszthelyi, 2006).

Results on hydroxamic acids are detailed in (Telegdi, 2004, Telegdi, 2005b, Rigó, 2005, Telegdi, 2007, Telegdi, 2008, Telegdi, 2010 and Raman, 2010). As the efficiency results presented in Tables 2O.5.6.1 and 2O.5.6.2 show, the molecular layers are capable of diminishing the corrosion rate.

Oleoyl hydroxamic acid and stearoyl hydroxamic acid in SAM layers were compared (Románszki, 2008), as well as decanoyl hydroxamic acid and octadecanoyl hydroxamic acid SAMs (Alagta, 2008) and dodecanoyl hydroxamic acid, octadecanoyl hydroxamic acid, 12-hydroxy octadecanoyl hydroxamic acid and a hydroxamic acid polymer (Deng, 2008). Results showed that in SAM layers of molecules with double layers, the anticorrosion as well as the antifouling efficiency decreases due to the disturbed conformation of the carbon chain.

Anticorrosion and antifouling activity has been parallel studied in the presence of phosphonic and hydroxamic nanolayers. When molecular films of these amphiphilic molecules cover iron and copper surfaces they can effectively control the corrosion and, at the same time, the microbial adhesion as shown in Table 2O.5.6.4. The presence of hydrophobic nanolayers decreases the surface energy and the number of adhered microorganisms is decreased by orders of magnitudes.

7.5.7 Amino acids

Arginine SAM coatings formed on a pure copper surface show a degree of anticorrosion effect in acidic solution (Zhang, 2009). According to EIS polarization measurements, the inhibitor efficiency of the layers reaches a maximum of 63%. The same research group investigated the inhibitor effect of histidine SAM coatings also under acidic condition (Zhang, 2010a, Zhang, 2010b). The anticorrosion efficacy of the SAM layers increased by up to 75% when iodine ion was also used.

7.5.8 Phosphonic acids

Phosphonic acid nanolayers have also been studied (1*H*,1*H*,2*H*,2*H*-perfluorodecyl phosphonic acid, 1-octyl-, decyl- and octadecyl phosphonic acids) (Hoque, 2009, Raman,

2010, Telegdi, 2005b, Rigó, 2005, Keszthelyi, 2006). This work showed that with increasing carbon length, the compactness of the surface SAM layer improves and the anticorrosion and antifouling effect significantly increases.

7.5.9 Sulfonic acid

A good example of protective sulfonic acid nanolayers is the 1-octadecyl sulfonic acid (Raman, 2010). Generally the sulfonic compounds do not form a well-ordered SAM layer (and are not applicable to LB layer preparation because of their high solubility in water) and as such are not used as anticorrosive coating.

7.5.10 Silane derivatives in layers

Silane derivatives in nanolayers have also been extensively studied as potential corrosion inhibitors. An example involves 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichlorosilane (Hoque, 2006). The efficacy is explained by the high hydrophobicity of the layer.

7.6 Self-healing corrosion- and biofilm formation inhibiting coatings using nano/microcapsules and nano/microspheres

7.6.1 The principle of self-healing

Self-healing is observed in biological systems. For example, in the case of scars forming on skin the damaged tissue regenerates. The microcapsule-driven self-healing of artificial coatings is simpler to such processes in living systems. Small hollow vessels, core-shell structured spheres (in the nano- or micron range) immobilize a specific glue-like fluid in the coating layer. In case of external or internal mechanical stimuli (cuts, crackings, scars) these containers break up within the paint matrix, and release their fluid content along the damaged site. The healing mechanism is finished when the liquid, 'healant', solidifies through drying or polymerization, forming a protective layer between the damaged coated substrate and the corrosive environment. Self-healing materials are a combination of initiators, catalysts, and co-monomers that are present in the environment, in the paint matrix or are released from other types of capsules embedded in the same coating (Ghosh, 2006, Wu *et al.*, 2008, Mauldin *et al.*, 2010, Samadzadeh *et al.*, 2010, Murphy *et al.*, 2010). Certain types of functional paints are slow-release coatings that contain active agents entrapped in a usually solid matrix-structured carrier. Slow-release is generally attributed to coating systems that require prolonged and continuous self-healing efficiency against corrosion or biodeterioration without the burst-out phenomena (the early-stage fast release of active agents). The objective of entrapment of active materials into microsphere matrices is to slow the release rate through the coating thus ensuring the long-lasting effect (Ghosh, 2006; Zheludkevich *et al.*, 2012).

7.6.2 Core-shell structures

There are two main types of carrier structures:

- capsules
- spheres

Capsules are spherical, hollow containers with an outer protective shell and inner core (active) material. Spheres also have a spherical structure but have a solid, usually

homogenous, chemical and physical composition with active materials dispersed within. Based on diameter, both are sorted into nano- and microcapsules/-spheres.

A broad spectrum of polymers are suitable for shell-formation: polyurethanes, polyesters, polyamides, melamine resins, polyureas, polysiloxanes, polyacrylates and its co-polymers (Podszun *et al.*, 2002), hydrolyzed polyvinyl acetate (or hydroxy/alkyl-cellulose derivatives), phenolic resin, urea- formaldehyde (Reybuck *et al.*, 2008), melamine-urea-formaldehyde resin (Tong *et al.*, 2010), silica gel, etc.

Slow-release microcapsules often consist of gelatin and a polyionic substance: gum arabic (Guarda *et al.*, 2011), gum acacia, (Miale *et al.*, 1981) polyphosphate, alginate, carboxymethyl-cellulose, carrageenan, ethylene/maleic/acrylic acid copolymers (Mihm *et al.*, 1995; Podszun *et al.*, 2002). Cross-linking agents are glutaraldehyde, tannic acid (Miale *et al.*, 1981), and shell-densifying quinone (Mihm *et al.*, 1995).

As core materials, hydrophobic tributyltin-chloride/fluoride (Miale *et al.*, 1981) or essential oils thymol, carvacrol (Guarda *et al.*, 2011), 4,5-dichloro-2-n-octyl-3(H)-isothiazolone (Hart *et al.*, 2009), 2-n-3(2H)-isothiazolone, benzisothiazolone, triphenyl-boronpyridine, Diclofuanide, Chlorothalonil, Irgarol, Folpet, Diuron (Reybuck *et al.*, 2008; Podszun *et al.*, 2002; Hart *et al.*, 2009) are applied. Tributyltin-derivatives have been banned since 2008 because of their toxicity (Dafforn *et al.*, 2011).

The most common core substances for self-healing systems are dicyclopentadiene and Grubbs catalysts (White *et al.*, 2001), epoxy resins (Zhao *et al.*, 2012; Liu *et al.*, 2012), diglycidyl ether bisphenol-A based epoxy resins with an imidazole hardener (Rong *et al.*, 2007), mercaptan compounds and cationic initiators BF₃.OEt₂ (Yuan *et al.*, 2008), vinyl functionalized poly(dimethylsiloxane) resins and platinum catalysts (Keller *et al.*, 2007), styrene (Wang *et al.*, 2008, Wang *et al.*, 2009), polythiol epoxy hardeners (Yuan *et al.*, 2008), reactive amines (McIlroy *et al.*, 2010), diisocyanate resins (Yang *et al.*, 2008), methyl(methacrylate) (He *et al.*, 2009). Its drying on air can be used in coatings contacted with air: linseed oil (Selvakumar *et al.*, 2012, Szabó *et al.*, 2011, Boura *et al.*, 2012, Nesterova *et al.*, 2012;), tung oil (Samadzadeh *et al.*, 2011), water-reactive silyl ester (García *et al.*, 2011). Shell materials are polyurethane, amino or phenolic resins, and silica.

7.6.3 Nano/microspheres

Micro- and nanospheres are dense polymeric matrices or porous, sponge-like structures with active substances dispersed in the matrix or loaded into the pores. Active components tend to leach in a moist environment. For anti-fouling purpose, biocides are encapsulated into various carriers: zinc-pyrithione in 2-10 nm silica aerogel particles (Wallström *et al.*, 2011), 3-iodoprop-2-ynyl N-butylcarbamate in porous silica microspheres (Sørensen *et al.*, 2010), silver nanoparticles in gelatinous microparticles (Szabó *et al.*, 2011), medetomidine in poly(methyl methacrylate) microspheres (Nordstierna *et al.*, 2010), medetomidine, seaine, Irgarol, tolylfluanid in poly(methyl-methacrylate) (Mok, 2010) and in hydroxystyrene homo and copolymer microspheres (Ghosh, *et al.*, 2003), 3-isothiazoline derivatives in acrylic microgels (Gold *et al.*, 2003), in acrylate, gum arabic, formaldehyde-melamine resin microparticles (Baum *et al.*, 2008) or adsorbed on the surface of carbon-, silica- and zeolite microparticles (Dai *et al.*, 2004; Aldcroft *et al.*, 2005).

Anti-corrosive self-regeneration is realized by slow, mostly pH-triggered release of inhibitors from micro- or nanoreservoirs (Shchukin *et al.*, 2007; Motornov *et al.*, 2010). Lately various compositions have been considered: cerium(III) in zeolite microparticles (Dias *et al.*, 2012), mercaptobenzothiazole in cerium molybdate hollow nanospheres (Montemor *et al.*, 2012), cerium

nitrate in zirconia nanoparticles (Zheludkevich *et al.*, 2005), triethanolamine in methacrylate-styrene nanoparticles (Choi *et al.*, 2012) and benzotriazole in mesoporous silica nanoparticles (Borisova *et al.*, 2011; Zheludkevich *et al.*, 2007).

7.6.4 Nano- and micro encapsulation techniques

Encapsulation methods all require the development of a solid layer around the effective materials (Samadzadeh *et al.*, 2010). Methods to achieve encapsulation can be divided into:

- chemical
- physical or physico-chemical processes

Each method has its advantages. Generally, physical techniques are faster and relatively simple compared to chemical ones. Chemical techniques have the advantage of resulting in a precisely tuned capsule structure that is especially applicable to slow-release systems. With chemical techniques, the formed shell is a chemically new material composed of former reactants, while physical methods are mostly based on phase separation of the shell material so that its chemical structure doesn't change during the process.

The following discussion considers chemical microencapsulation techniques. To prepare core-shell capsules, liquid core substances are emulsified in a non-miscible media, thus oil-in-water or water-in-oil micro or macro emulsions are often used. The shell-forming compounds are dissolved in the continuous phase (emulsion polymerization) or in both the continuous and non-continuous phase (interfacial polymerization) and throughout polymerization reactions (addition, condensation) they form a polymeric layer at the oil/water interface (Nesterova *et al.*, 2011).

When powder core materials are dispersed in a liquid phase, the shell may be developed on the surface by reactions similar to those in the case of liquid core droplets.

Preparation of solid matrix microspheres is carried out by dispersion polymerization. The components of the matrix material and the active substance are dissolved in the same liquid phase and then this liquid is dispersed in a non-miscible continuous liquid. The polymerization reaction takes place in the droplets.

Turning to physical or physio-chemical techniques, coacervation, sol-gel deposition, layer-by-layer deposition and solvent evaporation techniques with modifications can be used to prepare capsules as well as spheres. Simple coacervation is a phase separation phenomena that occurs when the solubility of a dissolved hydrocolloid is reduced. Complex coacervation (phase separation) happens also in a liquid phase when a charged polyelectrolyte is added to an oppositely charged component (Mihm *et al.*, 1995). Both processes are suitable for shell-deposition from an aqueous phase onto surfaces of oil droplets or solid powders. The coacervation method usually results in permeable, porous shells applicable to slow-release coatings (Grigoriev *et al.*, 2012).

Sol-gel deposition is a multi-step process: silica or metallic alkoxides hydrolyzed in aqueous media go through a condensation reaction with the elimination of water, providing a solid material (e.g. Stöber silica) that can be deposited onto oily surfaces or else forms solid matrix spheres. Layer-by-layer deposition is a method to fabricate thin layers of oppositely charged polyions on surfaces. With this process, one can deposit molecules or nanoparticles onto droplets to yield a shell with a well-defined structure (Sonawane *et al.*, 2012).

With the solvent evaporation technique, a solution of polymer with active agent is dissolved in a volatile solvent (Nordstierna *et al.*, 2010; Mok, 2010) and dispersed in an aqueous media to obtain a precise droplet diameter. The organic solvent is removed by heating in a vacuum.

If the active substance is solid, the remaining material is a solid matrix sphere with dispersed active agent. In the case of a liquid active material, by evaporating the solvent the liquid will be enclosed in the polymer as result of phase-separation. Fluid bed coating is a method for coating fluidized powder-like materials with vapours of shell material solution.

7.6.5 Single, dual, multi shelled capsules

Increasing the shell width of a capsule is necessary if the permeability or the mechanical stability of the layer is not satisfactory. Preparation methods for different layers may differ. Shells of slow-release microcapsules in solvent-based paints must resist the solvent but should be hydrophilic enough to ensure water-accessibility. This criteria can be fulfilled for example with a stable melamine-formaldehyde resin and a hydrophilic urea—resorcinol-formaldehyde combination (Reybuck *et al.*, 2008). It is also possible that shells formed by interfacial polymerization are mechanically stable though solvent stability is poor (e.g. polyurethane). A second or further layer (e.g. urea-resorcinol-aldehyde) can be deposited from the aqueous phase by emulsion polymerization, precipitation, or coacervation.

7.6.6 Characterization of microparticles

Size-distribution of particles can be determined by microscopy (optical or scanning/transmission electron microscopy (SEM, TEM)) or light scattering methods. Scaling shell wall thickness is also possible with SEM after proper sample preparation (Figs 2O.6.6a and 2O.6.6b). Surface characteristics e.g. morphology can be visualized by microscopes. For detailed information, atomic force microscopy is necessary. Specific surface area is usually calculated from gas adsorption results.

Characterization of mechanical stability is also possible with atomic force microscopy or nanoindentation (Su *et al.*, 2012; Lee *et al.*, 2012). The chemical structure of polymer-containing capsules is determined by differential scanning calorimetry with regard to T_g and thermal stability (Zhao *et al.*, 2012), Fourier-transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, and small and wide angle X-ray spectroscopy. The encapsulated substance can be quantified by X-ray and UV-VIS spectroscopy, microscopy, quantitative NMR methods (Nordstierna *et al.*, 2010). Further investigations on release properties generally involve liquid or gas chromatography, atomic absorption/emission spectroscopy etc.

7.6.7 Compatibility of microcapsules with paint components

The question of compatibility has two main points: stability of the capsules in liquid paint and the duration for drying of the layer. The stability of capsules in liquid paints is so called *in-can stability* which is demonstrated by the amount of released active material during storage, measured at 90 days and at a given temperature (Reybuck *et al.*, 2008). After applying the paint with capsules or spheres the coating should not contain inner strains or show visual disturbance. Cohesion between capsules and binder can be improved by surface modification or using shell material similar to the coating components e.g. sol-gel coatings with silica particles (Borisova *et al.*, 2011.).

7.6.8 Release of the active substance

The release mechanism of encapsulated or encaged corrosion and fouling inhibitors varies with the structure of the carrier (Fig.2O.6.8.1). Matrix type particles placed in an aqueous environment with given parameters (temperature, pH, ionic strength) take up a certain

amount of water depending on their structure and this permits continuous leaching of the active materials by diffusion. The timing and release rate can be controlled through a carefully constructed composition.

From core-shell capsules self-healing materials are released upon rupture of the capsule shell (Figs 20.6.8.1 Corrosion inhibitors and antifoulants leach out hence shell permeability should be adjusted by the ratio of hydrophobic-hydrophylic monomers or shell thickness. Melamine-formaldehyde resin forms very stable shells with low permeability to both solvents and water (Reybuck *et al.*, 2008).

Antifoulants from paint leach into an aqueous environment, repulsing or destroying organisms and should therefore be added to the cover paint layer (Fig. 20.6.8.2). Release characteristics are investigated by a comparison of paints with free and encaged active components in deionized or model water (Mok, 2010) using chromatography (Guarda *et al.*, 2011), UV-visible spectrophotometry (Wallström *et al.*, 2011), radioactivity measurements with isotope labeling (Nordstierna *et al.*, 2010, Mok, 2010) and atomic absorption spectroscopy.

Release rates from capsules and solid spheres, as well as from paints, decreases with time though the blending of encapsulated and free substances in the paint and may lead to an equilibrated flux of the active agent (Reybuck *et al.*, 2008).

Self-healing material stays adhered within the wounds of the paint. To preserve the continuity of the coating under wet conditions, drying of healing liquid must be accelerated. Efforts have been made towards combinations of healing agents and corrosion inhibitors reducing the decay of metal substrate during the healing process (Selvakumar *et al.*, 2012; Kumar *et al.*, 2006).

7.7 Assessing the efficiency of coatings

On antifouling coatings, microbial adhesion tests, optical monitoring, weight-growth rate measuring, raft or yacht tests (Wallström *et al.*, 2011), laboratory tests with natural water or model water (Wallström *et al.*, 2011) are performed. For investigation of corrosion phenomena, visual observations, salt spray tests, electrochemical measurements, and elemental analyses are usually carried out.

7.7.1 Surface visualisation

Macro- and microscopic visualization of coatings gives information on anticorrosive and antifouling efficacy. Foulants and corrosion products on coated surfaces can be easily observed by sight; microbes in thinner biofilms should be stained with dyes for fluorescence microscopic visualization. Visibility of self-healing agents encapsulated or released can be enhanced by colorants and pigments for optical monitoring; contrast materials for element spectroscopy, and energy dispersive X-ray spectroscopy help the identification of biofouling. For detailed mapping of the corrosion and fouling site, photoelectron-spectroscopy and scanning probe microscopy is also used.

7.7.2 Electrochemical techniques

Electrochemical techniques have great importance in the characterization of anticorrosive coatings and are able to determine the corrosion rate and permeability of the paints in a

corrosive environment. Electrochemical impedance spectroscopy (EIS) measures the impedance of a substrate through damaged or undamaged coating as a function of frequency and time (Montemor *et al.*, 2012). EIS spectra have relevance in the determination of global corrosion mechanisms. Additionally, electrochemical techniques may be used to measure the corrosion of metals with organic coatings using, for example, the scanning vibration electrode and scanning Kelvin probe techniques (Grundmeier *et al.*, 2000; Valentinelly *et al.*, 2002; Deflorian *et al.*, 2003; Fedrizzi *et al.*, 2003).

It is important to follow and quantify the corrosion phenomenon of coatings with encapsulated materials that act only in the case of damage (thin cracks or scratches). Local corrosion along coating discontinuities can be monitored by SEM (Montemor *et al.*, 2012) and scanning electrochemical microscopy (Pilbáth *et al.*, 2012; Zheludkevich *et al.*, 2005). The current of the scanned surface over a scratched coating is decreased significantly by the presence of microcapsules in the coating (Fig.20.7.2.1).

7.7.3 Microbiological methods

The antimicrobial efficiency of the coating can be determined by agar plate tests. The released biocide will inhibit the cell-growth in a growing halo around the coated substrate. This halo is called the zone of inhibition (Zoi), and its size is representative of the efficiency of the coating. An important microbiological method is the determination of minimal inhibitory concentration when the biocide visibly inhibits the microbial growth after an overnight incubation (Andrews, 2001). Liquid media test show the inhibition effect of microparticles or paints submerged in inoculated aqueous media.

7.7.4 Testing the efficacy of self-healing coatings in a corrosive environment

A corrosive environment is mimicked with a test medium that contains electrolyte (perchlorate, sulphate, etc.) and pH-controller/corrosive compound (perchloric acid, chloride ion, oxygen, salts). Liquid healants in coatings need time to set after release, otherwise no sealing efficacy will be observed. The advantage of this solution is that once the solid layer is set, the metal surface is protected. In some cases the active inhibitor slowly releases a sponge-like capsule when a certain corrosive pH (trigger) is reached in the crack or scratch. Their disadvantage is that efficiency decreases in time with the exhaustion of the carrier capsules.

7.7.5 Efficacy of slow release particles in paints on microbial accumulation in the presence of micro- and macroorganisms

Encapsulation of thymol and carvacrol leads to controlled release efficiency against *Escherichia coli*, *Staphylococcus aureus*, *Listeria innocua*, *Saccharomyces cerevisiae* and *Aspergillus niger* (Guarda *et al.*, 2011). Against fungus *Cladosporium cladosporioides* isothiazolinon loaded carriers in paint films retain more biocidal activity after leaching than those containing free biocides (Edge *et al.*, 2001)

The controlled release from paint films with 3-Iodo-2-propynyl-butylcarbamate (IPBC) encapsulated in microparticles as well as with IPBC in model solution has been tested and resulted in prolonged release of encapsulated biocide compared to IPBC in reference solution (Sørensen *et al.*, 2010). Raft and yacht tests have shown that paints with acrylic resin and hydrogenated rosin binder, embedded with zinc pyrithione loaded silica aerogel nanospheres show extended water uptake and the coating shows similar efficacy compared to commercial paints (Wallström *et al.*, 2011). In laboratory tests paints with encapsulated silver nanoparticles showed sustained silver release and more efficient anti-fouling effect than those with free silver compounds (Szabó *et al.*, 2011). When the antifouling silver was not dispersed in microspheres but distributed directly in the paint, its dissolution rate increased and the antifouling time-span decreased. The silver in the solid matrix guaranteed a prolonged

inhibition against microbial deposition (Fig. 20.7.5.1a-d). Medetomidine in poly(methyl methacrylate) spheres shows a slower and balanced release for both water and solvent based wall paints (Nordstierna *et al.*, 2010).

7.8 Conclusion

In this chapter a broad range of surface protection by different mono- and microcoatings against corrosion and microbial adhesion was discussed. The selection of molecules, nano- and microparticles and coatings depends on the solid to be protected from electrochemical and microbial corrosion as well as from the environment (pH, temperature, dissolved ions etc.). The adhesion of Langmuir-Blodgett and self assembled molecular layers to solid surfaces is determined by the metal surface state. Some groups of molecules prefer an oxide layer where they are chemisorbed. Others can only adhere to pure metals. These densely packed nanolayers can prevent the penetration of aggressive ions to the metal surface. Anticorrosion and antifouling activity increases with increasing surface hydrophobicity. Reduction of surface energy results in increased repellent activity.

Realization of coatings with micro or nanocontainers is still in an early development stage but there are promising results based mostly on electrochemical measurements which were carried out in acidic or neutral media. Slow-release systems with good corrosion resistance under acidic pH were obtained using benzotriazole in mesoporous nanoparticles embedded into SiO_x/ZrO_x sol-gel coating on AA2024 alloy (Borisova *et al.*, 2012). Benzotriazole in polyelectrolyte layers formed around ZnO nanoparticles mixed in alkyd resin on mild steel showed good corrosion resistance under pH 3-7 with sustained inhibitor release (Sonawane *et al.*, 2012). Zheludkevich reported the modification of sol-gel films applied on AA2024 alloy with cerium nitrate containing zirconia nanocontainers (Zheludkevich *et al.*, 2005) and with benzotriazole in polyelectrolyte layers of silica nanoparticles (Zheludkevich *et al.*, 2007). Both films were resistant to corrosion and the barrier properties were not reduced by the addition of nanocontainers. Epoxy primers on galvanized steel, containing a mercaptobenzthiazole inhibitor in cerium molybdate showed weaker barrier properties but good results during longer exposure. The same inhibitor in layered double hydroxide nanoparticles performs well during early exposure as the barrier properties were not affected (Montemor *et al.*, 2012). Attempts were made towards simultaneous encapsulation of corrosion inhibitors and film-forming healing agents (eg. CeO₂ and Cr₂O₃ nanoparticles in linseed oil). These capsules improved the self-healing of epoxy resin applied on mild steel (Selvakumar *et al.*, 2012).

Self-healing driven by film-forming of an encapsulated liquid is being widely investigated. There are encouraging results on self-healing of epoxy resins on AA2024 alloys by water-reactive silyl ester in urea-formaldehyde shells (García *et al.*, 2011), sol-gel silica coatings on AA2024 alloys by methyl methacrylate in silica gel microcapsules (He *et al.*, 2009), epoxy resins on carbon steel by epoxy binders in epoxy-amine shells (Liu *et al.*, 2012), epoxy resins on carbon steel by linseed oil in urea-formaldehyde shells (Boura *et al.*, 2012), and epoxy resins on carbon steel by tung oil in urea-formaldehyde shells (Samadzadeh *et al.*, 2010). Liquid paints with capsules are also an active area of research, with most of the coatings applied with brush or roller. Spray-applying is not yet in practice (Keller *et al.*, 2007). Capsules reduce adhesion when embedded directly onto a layer near to the metal surface (Keller *et al.*, 2007), with the exception that sol-gel particles bond covalently onto oxide layers. In certain cases inhibitors change the coating structure thus their encapsulation improves barrier properties (Dias *et al.*, 2012).

7.9 References

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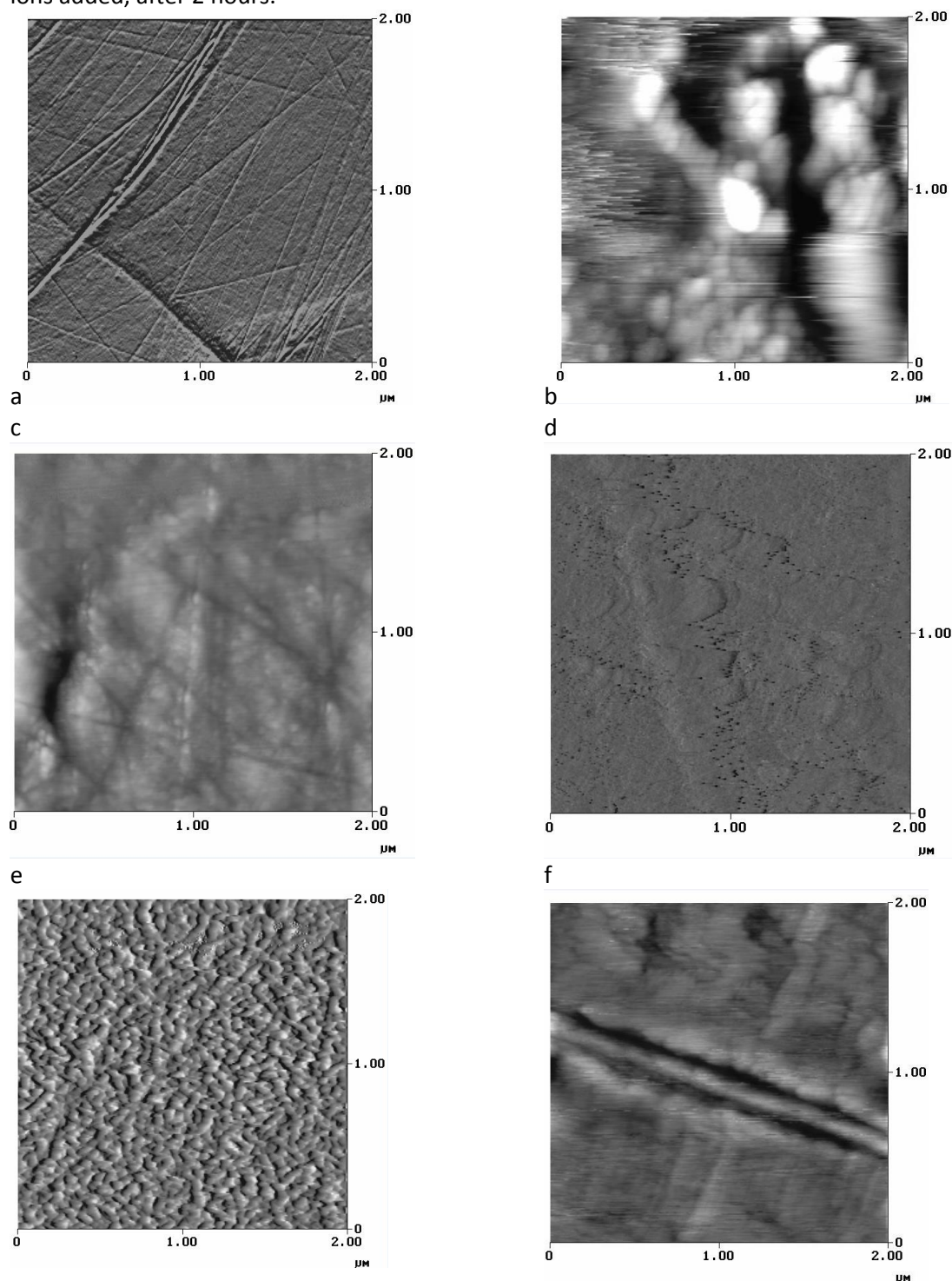
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Figures and captions

Fig. 20.2.2.1a–g Anticorrosion effect of *N,N*-diphosphonomethyl glycine (INH) alone and together with cations on the corrosion of mild steel, visualized by AFM; a: mild steel in air; b: mild steel in perchlorate solution, pH=7, after 20 min; c: INH added alone, after 1 hour; d: INH + Ba²⁺ ions added, after 1 hour; e: INH + Zn²⁺ ions added, after 1 hour; f: INH + Sr⁺ ions added, after 1 hour; g: INH + Sr²⁺ ions added, after 2 hours.



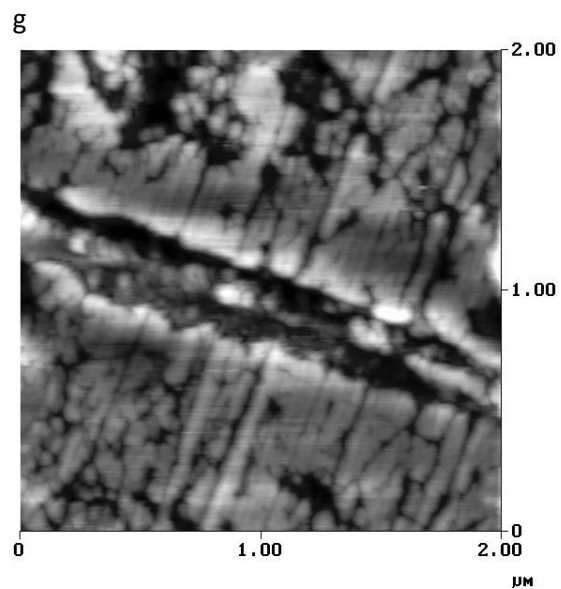


Fig. 20.4.1a–b Bacterial cells affected by chemicals; a: partly destroyed cells with coagulated plasma; b: total lyses of a cell

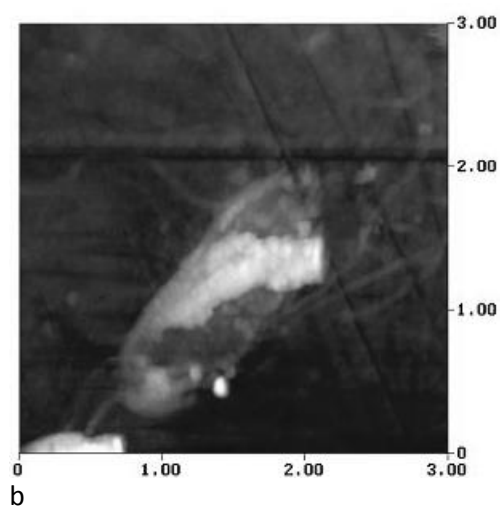
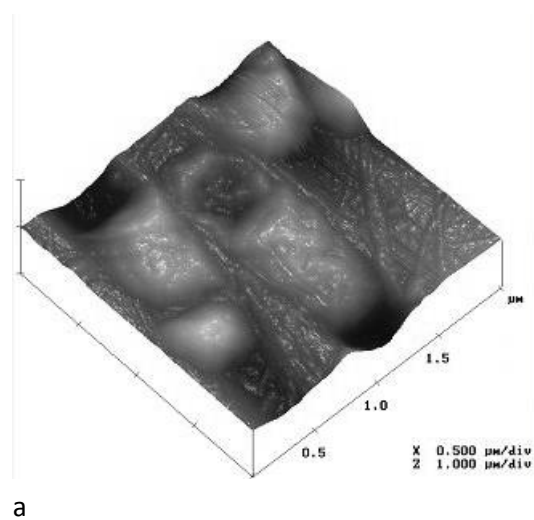


Fig. 20.4.2 Some amphiphilic compounds used in LB and SAM preparation

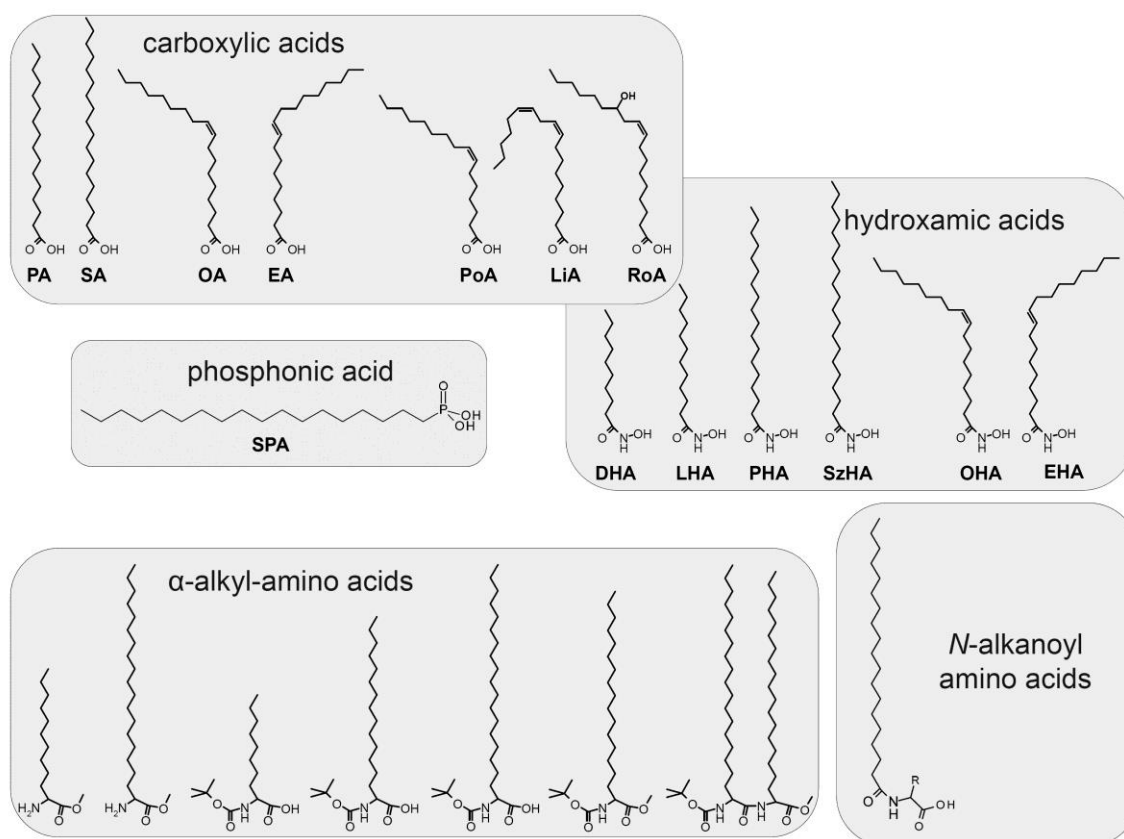
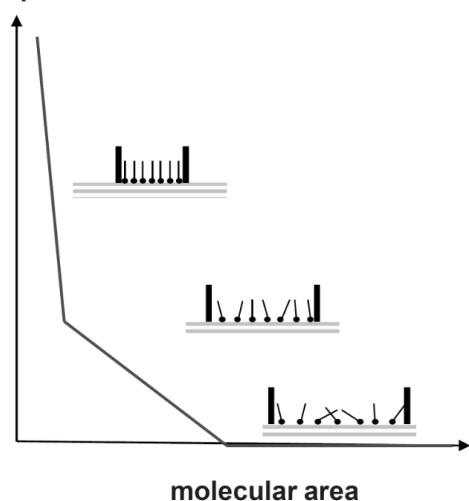


Fig. 20.4.1.1 A generalised isotherm of a Langmuir film and the orientation of film-forming molecules at different compression stages

surface pressure



molecular area

Fig. 20.4.3.1 Order and disorder in SAMs: SFS spectra of a saturated (palmitic, PA) vs. an unsaturated (oleic, OA) carboxylic acid monolayer on glass and schematic representations of the orientation of molecules within the layers

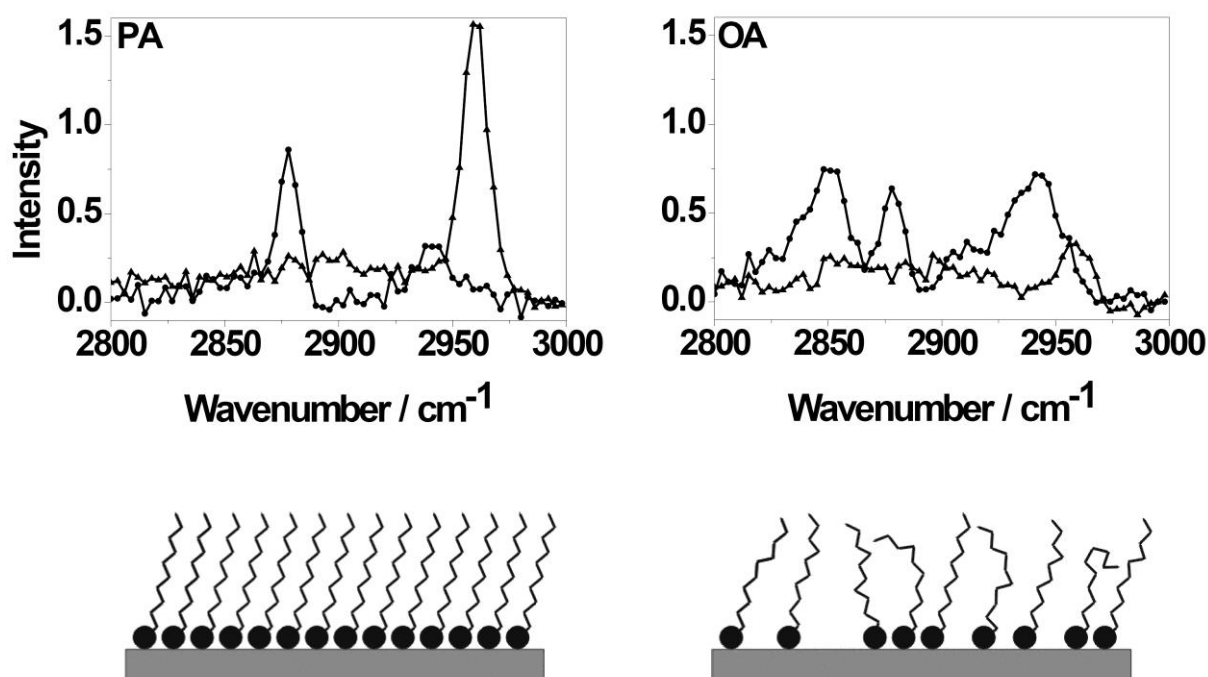


Fig. 20.4.4.6.1 RAIRS spectra of SAMs of hydroxamic acids with various chain lengths (10–18). Intensities of the detected characteristic methyl and methylene peaks increase with increasing chain length.

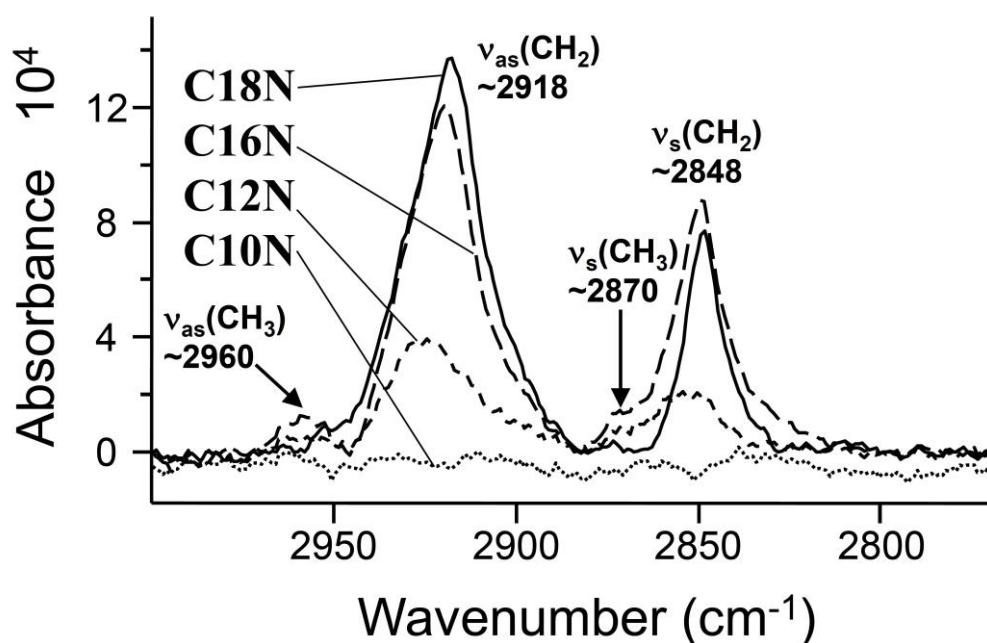


Fig. 20.4.4.6.2a–b AFM images of copper surface after immersion in NaCl solution; a: bare copper surface after 20 min.; b: copper surface protected by a SAM layer of octadecanohydroxamic acid after 60 hours. Scanned areas: $50 \times 50 \mu\text{m}^2$; height/depth scale: $\pm 1000 \text{ nm}$.

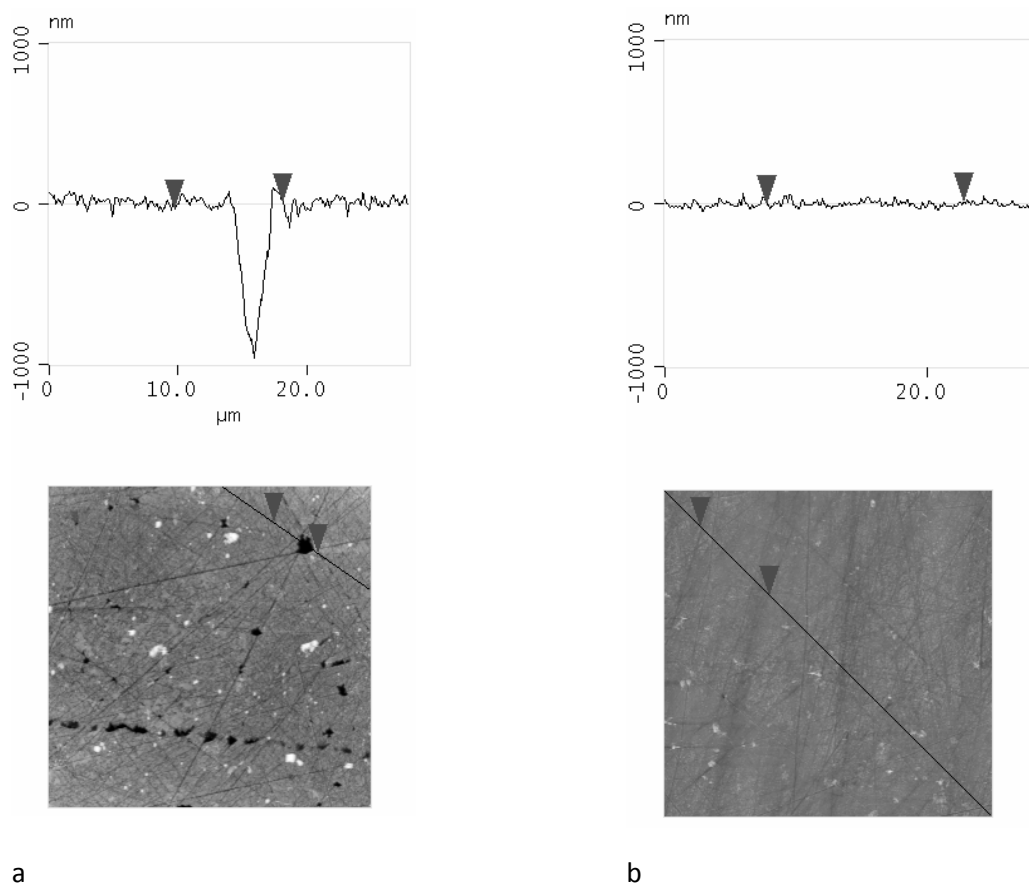


Fig. 20.5.6.1a–b Scanning electron microscope images of urea–formaldehyde core-shell capsules with diameter around $80 \mu\text{m}$. Intact (a) and (b) broken capsule, revealing shell thickness.

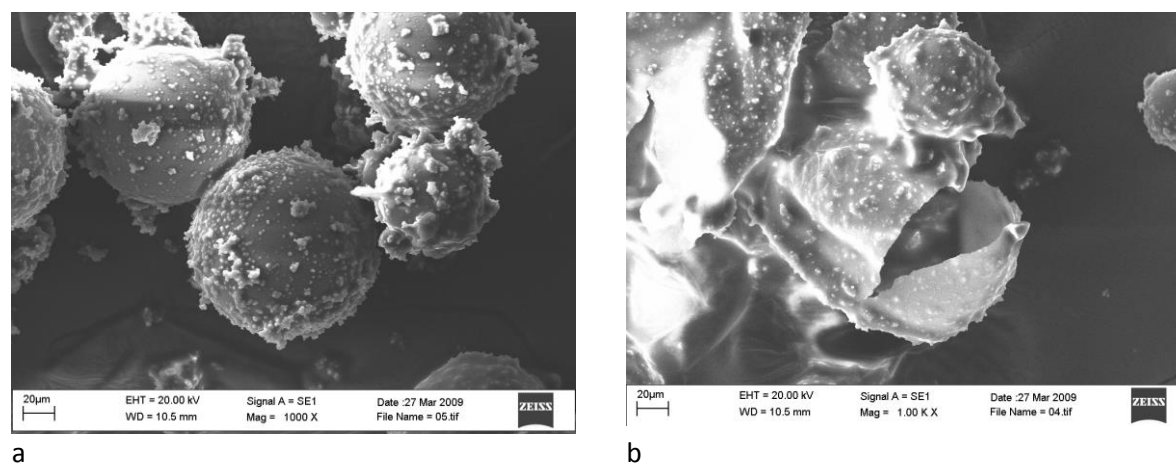


Figure 20.5.8.1 Illustration of structure and release mechanism of micro-containers.

Core-shell capsule with permeable shell, slow-release by diffusion (A); core-shell capsules with dense shell, release at rupture of capsule wall (B); solid matrix or porous sphere, slow release by diffusion (C).

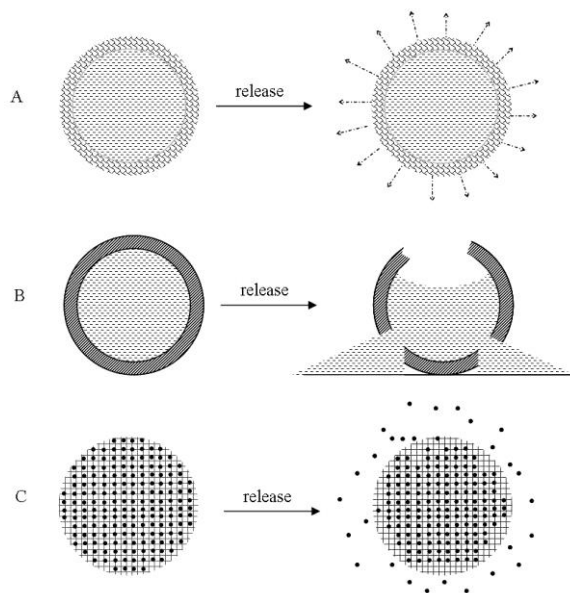


Fig.20.5.8.2 Illustration of coatings with microcapsules and microspheres. For anti-corrosion purpose, micro- or nanocarriers are embedded in the primer: core-shell capsules with self-healing liquid (A), slow-release spheres with homogenously dispersed inhibitor (B). For anti-fouling purpose, carriers are in the top coat: slow-release spheres (C) and core-shell capsules with permeable shell (D).

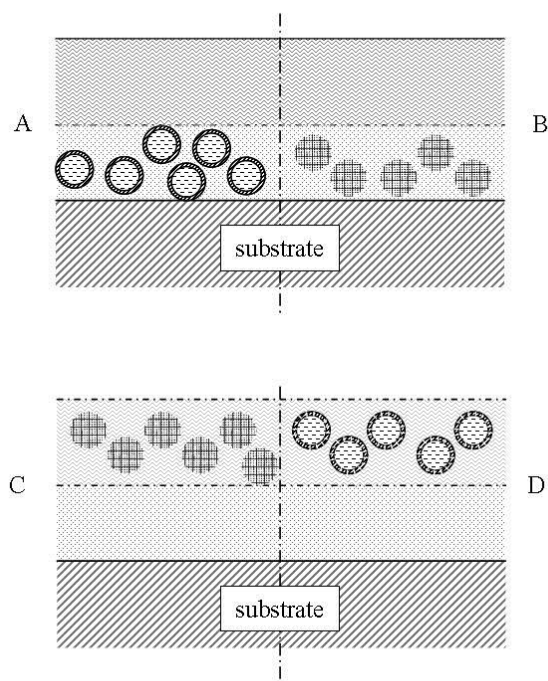


Fig. 20.5.9.2.1 Corrosion current measured by scanning electrochemical microscope across the scratches on coating without (○) and with (●) microcapsules.

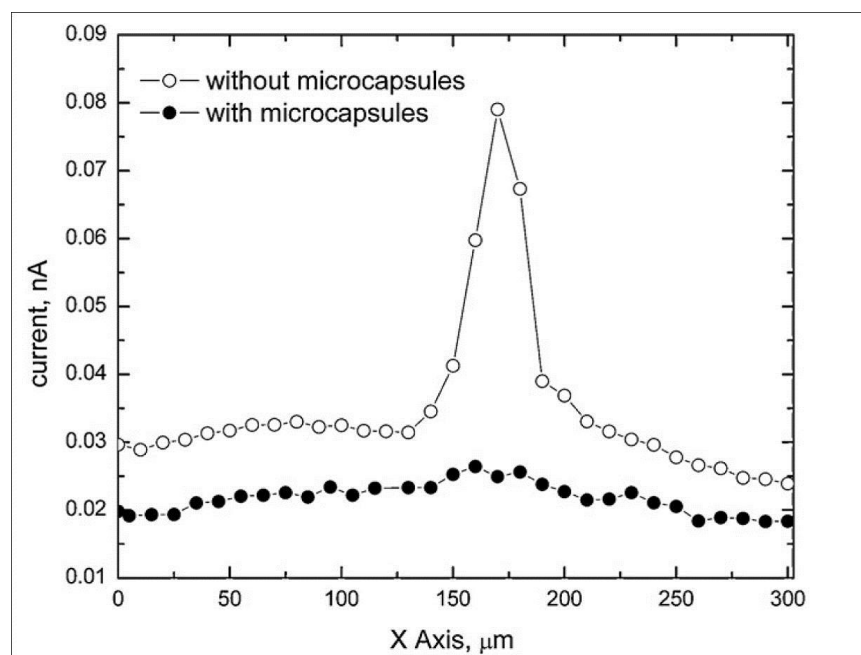
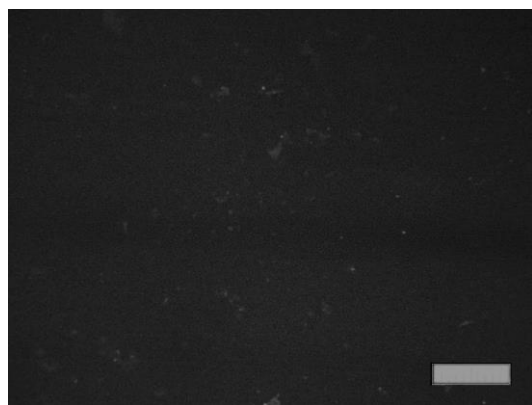
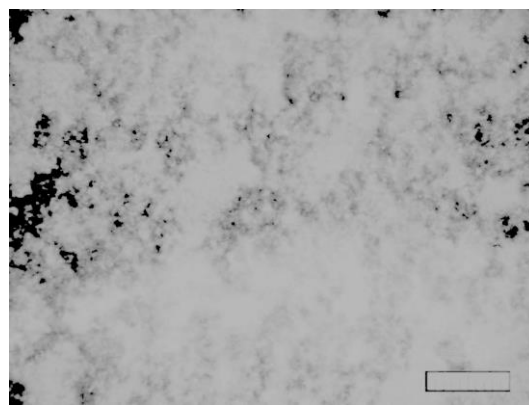


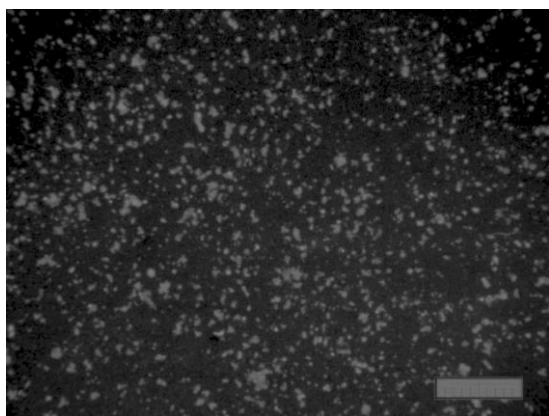
Fig. 20.5.9.5.1a–d Biofouling on coated mild steel surfaces dipped into natural water; a: coated surface before experiment; b: coated surface without additive, after 27 weeks; c: coated surface with dispersed silver compound, after 27 weeks; d: coated surface with microspheres that contained silver nanoparticles, after 27 weeks.



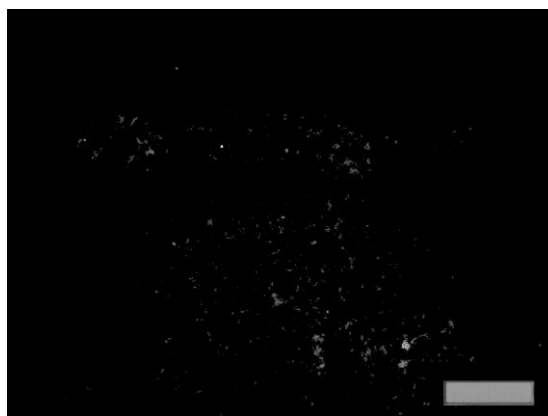
a



b



c



d

Tables and table captions

Table 20.4.1.1 The effect of temperature on the collapse pressure (mN/m) of hydroxamic acid Langmuir films

$C_n\text{HA}$	20 °C	25 °C	30 °C
$C_{16}\text{HA}$	38	34	27
$C_{18}\text{HA}$	46	37	31

Table 20.4.1.2 The effect of copper (II) ions present in the subphase on the molecular area ($\text{\AA}^2/\text{molecule}$) values of two α -amino acid derivatives, *N*-(*t*-butoxycarbonyl)-2-hexadecyl-glycine methylester (AA16) and *N*-(*t*-butoxycarbonyl)-2-octadecyl-glycine (AA18)

subphase	AA16		AA18	
	A_c	A_0	A_c	A_0
water	48.3	50.8	23.9	27.1
1 mM CuAc_2	43.4	48.5	19.7	24.4

Table 20.4.4.6.1 Influence of SAM layer formation on anticorrosion efficiency (R_p : polarization resistance; film-forming compound: hexadecanohydroxamic acid; medium: 0.1 M NaClO_4 ; temperature: 25 °C).

EIS after	→	1 h	20 h
R_p [$\text{k}\Omega \cdot \text{cm}^2$]			
SAM formation time			
5 min		5	15
15 min		106	305
60 min		2564	8596

Table 20.4.4.6.2 Polarization measurement: Anticorrosion efficiency of Langmuir–Blodgett films deposited onto iron (E_{corr} : corrosion potential; j_{corr} : corrosion current density; η : anticorrosion efficiency; medium: 0.1 M NaClO_4 , pH = 7; temperature: 25 °C; C18P: 1-phosphono octadecane; C18N: octadecanohydroxamic acid).

iron	E_{corr} [mV]	j_{corr} [$\mu\text{A}/\text{cm}^2$]	η [%]
blank	−412	2.36	-
with C18P LB film	−268	0.13	94
with C18N LB film	−251	0.09	96

Table 20.4.4.6.3 Polarization measurement: Anticorrosion efficiency of SAM layers deposited onto copper surface (E_{corr} : corrosion potential; j_{corr} : corrosion current density; η : anticorrosion efficiency; medium: 0.1 M NaClO_4 , pH = 7; temperature: 25 °C; C10N: decanohydroxamic acid, C12N: dodecanohydroxamic acid; C16N: hexadecanohydroxamic acid; C18N: octadecanohydroxamic acid).

copper	E_{corr} [mV]	j_{corr} [$\mu\text{A}/\text{cm}^2$]	η [%]
blank	-26	0.91	-
with C10N SAM	-36	0.13	76
with C12N SAM	-38	0.17	81
with C16N SAM	-39	0.16	82
with C18N SAM	-40	0.14	85

Table 20.4.4.6.4 Correlation between the surface energy of bare and LB-coated copper and iron surfaces and the number of adhered microorganisms (C18N: octadecanohydroxamic acid; C18P: 1-phosphono octadecane).

	Surface energy [mJ/m ²]	Surface density of microorganisms in biofilm [cell/cm ²]
iron	62.99	5.2×10^5
+C18N LB monolayer	25.06	3.6×10^3
+C18P LB monolayer	42.39	1.6×10^5
copper	56.67	1.2×10^5
+C18N LB monolayer	25.66	6.8×10^2
+C18N LB multilayer	21.28	1.7×10^2