

## **Protective organic coatings with anticorrosive and other feedback active features: micro- and nanocontainers based approach**

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### **ABSTRACT**

Development of materials possessing the ability to recover their main function(s) in response to destructive impacts is today one of most rapidly growing fields in the material science. In particular, protective organic coatings with the features to heal or restore their protective function autonomously are of great interest in fighting surface deterioration processes like corrosion, biofouling and other affecting metallic structures.

Embedding of micro- and nanocontainers in protective coatings is nowadays frequently used technique to provide them one or several feedback active functionalities. Depending on containers morphology and active agent(s) filled, coatings with specifically aimed self-recovering functionalities (anticorrosive, water-repelling, antifouling etc.) or multifunctional coatings can be created.

In the present paper, different types of containers for self-recovering functional coatings synthesized by use of mesoporous nano- and microparticles or on the emulsion basis are presented. L-b-L polyelectrolyte deposition, interfacial polymerization, surface precipitation, Pickering emulsions and in-situ emulsion polymerization were utilized for the preparation of nano- or microscaled containers. Morphology of containers, efficiency of encapsulation and kinetics of active agents release were investigated using modern techniques such as T-SEM, Cryo-SEM etc.

Incorporation of containers in the coating matrix was followed by the experimental modeling of external impacts leading to the simultaneous containers damage. Subsequent release of the active agent at the affected site caused the active feedback of the coating and self-recovery of its specific protective function. The advantages of novel container based protective coatings as compared to conventional ones are illustrated by corrosion tests results according to ASTM Standard B 117.

Key words: Nanoscale materials, Self-healing, Coatings, Corrosion, Smart materials, Multifunctional

### **INTRODUCTION**

The concept of engineering materials possessing the ability to re-establish their function(s) after damage autonomously has been widely developed in the last three decades inspired by the self-restoring and self-protecting features of mammalian skin and some other tissues. Proposed since the early 1990s [1, 2] and elaborated initially for the self-repair of materials integrity in the bulk [3], this idea was further transferred to interfacial phases first of all to anticorrosion coatings for metal substrates [4 –

7]. The specific design of the material structure on the micro- or nanolevel determines its active feedback behaviour. Correspondingly, several new approaches to fashion the fine structure of self-healing materials – containers based, network based (vascular) and intrinsic [8] – were proposed. Because of its universality and high variability in realization, approach connected with the incorporation of micro- or nanoscaled containers loaded with diverse active agents, in the material matrix, becomes now increasingly popular. These agents can be released upon the action of various factors working simultaneously as opening triggers for the containers that enable the active feedback of the entire system.

In the bulk materials, so-called sealing agents are typically used for the encapsulation in the containers providing the material bulk the recovering of the mechanical integrity and its mechanical properties [3]. Therefore, containers used for this purpose should have enough encapsulated self healing material to fill up at least partially the bulky crack areas in the material interior and can be quite large especially compared with the typical thicknesses of conventional polymeric anticorrosive coatings.

Following the same paradigm in the almost two-dimensional case of coatings, one has on the contrary to account for intrinsic limits for the highest possible volume of encapsulated sealing agents. On the one hand, this volume is closely related to the size of containers. On the other hand, their size is of crucial importance for their applicability in the coatings: only containers with size of several times smaller than the coating thickness can be incorporated without disturbing its integrity. For the quantitative estimation of sealing capacity of container based protective coating, let us imagine the rectangular scratch with the width  $L$  on the protective coating with thickness  $H$  and depth  $D$  approaching the metal substrate (see Fig. 1).

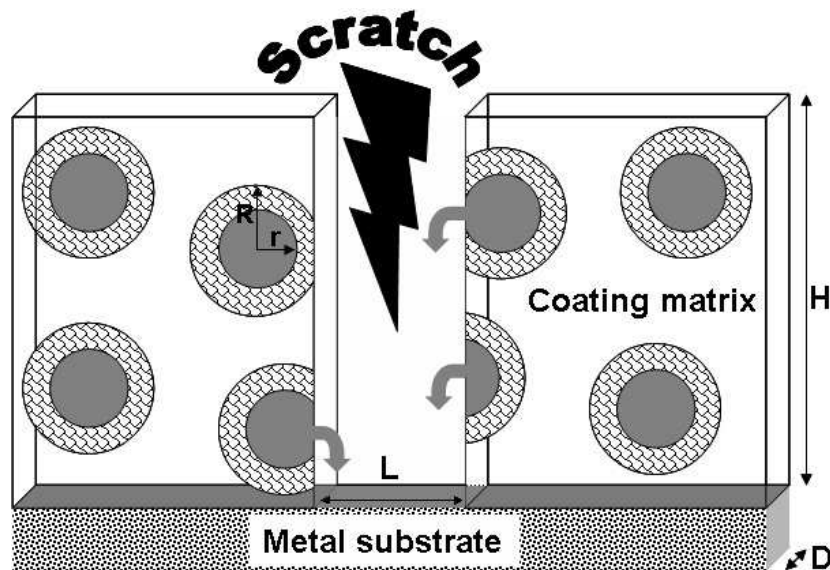


Figure 1. Illustration of the scratch propagation along the protective container based coating on the metal substrate affecting the embedded containers

This coating contains volume fraction  $\phi$  of monodisperse spherical core-shell containers with the size  $2R$  and core radius  $r$ , which are homogeneously distributed in the coating matrix. Obviously, only containers located at position  $x \leq r$  related to each scratch face will be injured by this scratch. Therefore, the risky volume close to the scratch can be expressed as

$$V = 2 \cdot H \cdot D \cdot r \quad (1)$$

where the total volume of containers within this volume is

$$V_C^t = 2 \cdot H \cdot D \cdot r \cdot \varphi \quad (2)$$

Correspondingly, number of containers  $N_c$  within this volume may be found from the ratio

$$N_c = V_C^t / V_c^1 = \frac{2 \cdot H \cdot D \cdot r \cdot \varphi}{4/3\pi \cdot R^3} \quad (3)$$

Taking into account the amount of the encapsulated sealant in the single container and their number expressed by eq. (3) one gets the total amount of sealant encapsulated in all containers within the damaged volume as

$$V_s^t = \frac{2 \cdot H \cdot D \cdot r^4 \cdot \varphi}{R^3} \quad (4)$$

This sealant can only fill the volume fraction of scratch  $\alpha$

$$\alpha = \frac{V_s^t}{V_{Scr}} = \frac{2 \cdot H \cdot D \cdot r^4 \cdot \varphi}{R^3 \cdot H \cdot D \cdot L} = \frac{2 \cdot r^4 \cdot \varphi}{R^3 \cdot L} \quad (5)$$

If the container shell thickness  $\delta = R - r$  is small enough the radii of container and of its core become almost equal, i.e.  $R \sim r$ . This allows the simplification of eq. (5) to the form

$$\alpha = 2 \frac{R}{L} \cdot \varphi \quad (6)$$

Analysis of this relation shows that for reasonable volume fraction  $\varphi = 0.1$  of containers with the diameter  $10 \mu\text{m}$  and negligible shell thickness, the complete sealing of damage ( $\alpha = 1$ ) caused by scratch is only possible for the scratches with widths not more than  $1 \mu\text{m}$ , i.e. only submicrometric scratches can be sealed completely. Defects of essentially larger size, much more frequently occurring during service life of a typical protective coating, can not be sealed even partially at practical implementation of concept of the container based protective coatings. These restrictions predestine the predominant use of protective agents for the containers loading (e.g. corrosion inhibitors) instead of sealing ones.

Efficiency of encapsulated inhibitor to protect the bare substrate surface freshly created by the scratch can be shown in the following estimation. Let us assume the spherical containers with  $R = 1 \mu\text{m}$  and  $\varphi = 0.05$  filled with an inhibitor with a molecular weight ( $M_w$ ) of  $500 \text{ g/mole}$  and possessing a density  $\rho$  of  $1 \text{ g/cm}^3$ . Using the same formalism as above, one can easily calculate that for the scratch with the width  $L$  on the coating having the thickness  $H$ , the maximal value of inhibitor adsorption on the scratch surface can be expressed as

$$\Gamma_{\max} = \frac{2 \cdot H \cdot R \cdot \rho \cdot \varphi}{M_w \cdot L} \quad (7)$$

In a quite realistic case of  $H = 70 \mu\text{m}$ , one obtains  $\Gamma_{\text{max}} = 1.4/L \mu\text{mole/m}^2$ . In other terms,  $\Gamma_{\text{max}}$  values of some millimoles per square meter can be obtained for typical millimetre-range scratches. This value is some orders of magnitude higher than typical saturation adsorption values  $\Gamma_{\infty}$  observed for organic inhibitors [9, 10] showing that even larger centimetre-wide damages of the coating surface can be safely protected by the inhibitor released from containers.

Thus, it is better to use here the term “self protecting” [11] instead of “self healing” because the physical integrity of coatings is rather not recovered during the protective action of the encapsulated inhibitor although the anticorrosion protective function of the coating in relation to the metallic substrate is re-established.

The conventional protective organic coating is as a rule a multilayer structure where at least some layers (most often – primer and topcoat layers) function as barrier from corrosive factors as well as from charge and mass transfer occurring during corrosion process. This polymeric protective system is however not robust enough to withstand diverse damaging impacts first of all of mechanical origin (scratches, abrasions, dents etc.) that can occur within its service life. Being damaged, such a passive coating can not provide satisfactory resistance against corrosives at the injured site and the corrosion development becomes unrestricted.

Most pronounced difference of container based self-protecting coatings from conventional ones is connected with their active feedback ability. First attempts to impart this feature to protective coatings were however realized even earlier by the most obvious direct doping of the passive protective coatings with corrosion inhibitors [12 – 16]. This type of coatings can be therefore considered as some kind of intermediate solution between classical passive and novel container based active feedback coatings. Straightforward incorporation of inhibitor in the matrix of passive coating led however in many cases [15, 16] to numerous complications due to the specific physicochemical properties of various inhibitors and negative interactions between them and the other components of the coating composition. As typical shortcomings of such a system, the deterioration of barrier properties of the coating matrix, premature leakage of incorporated inhibitor or its partial deactivation have to be mentioned. In contrast, the prior encapsulation of inhibitor(s) in nano- or microcontainers with their subsequent incorporation into coating not only allows avoiding these drawbacks but also can confer on it some additional benefits related to special construction of containers shells like specific stimuli-responsive properties.

As one can see, micro- or nanocontainers with the shells providing the release triggered on-demand is the key element of new self protecting coatings. Thus, further parts of this work are concerned with types of containers used in novel coatings, methods of their preparation, their morphology and release properties, distribution in coating matrices as well as with the functionalities of novel container based protective coatings.

## **Types of containers and methods of their preparation**

Two main types of nano/microcontainers were used for incorporation in the matrix of novel self protecting coatings: Containers with porous ceramic core impregnated by inhibitor and then enveloped by stimuli-responsive polyelectrolyte (PE) shell and; Polymeric and composite containers possessing inhibitor-rich core and stimuli-responsive shell prepared on the basis of direct or inverse emulsions. Both types of containers have their specific features that should be taken into account at preparation, loading and incorporation steps and will be discussed in more detail below.

### **A. Containers with porous or hollow ceramic core**

For fabrication of these containers the synthesized or naturally occurring mesoporous or hollow micro- or nanoparticles are utilized. Some examples of applied particles are given in the Figure 2. Independently from their chemical nature or natural or artificial origin, ceramic particles always serve as robust scaffold for the next steps of containers build-up and play simultaneously the role of sponge-like reservoirs that can be loaded by diverse active agents, in particular, by corrosion inhibitors. The total



volume of pores or cavities available for the loading can vary from 15 vol% for halloysite nanotubes (HS) to almost 70 vol% for highly porous silica particles.

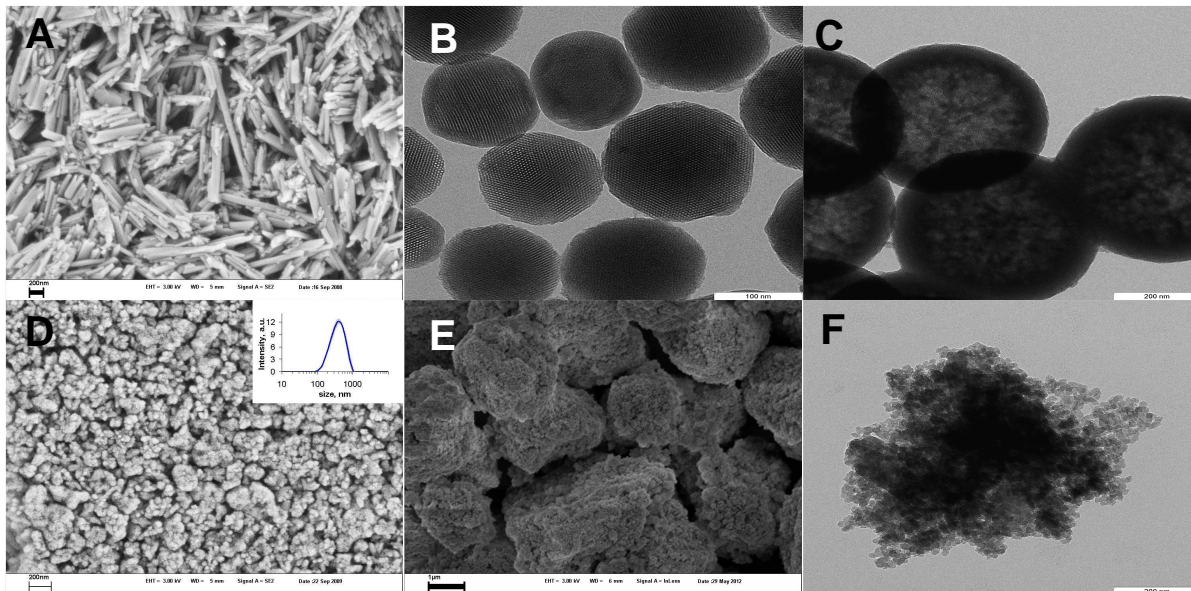


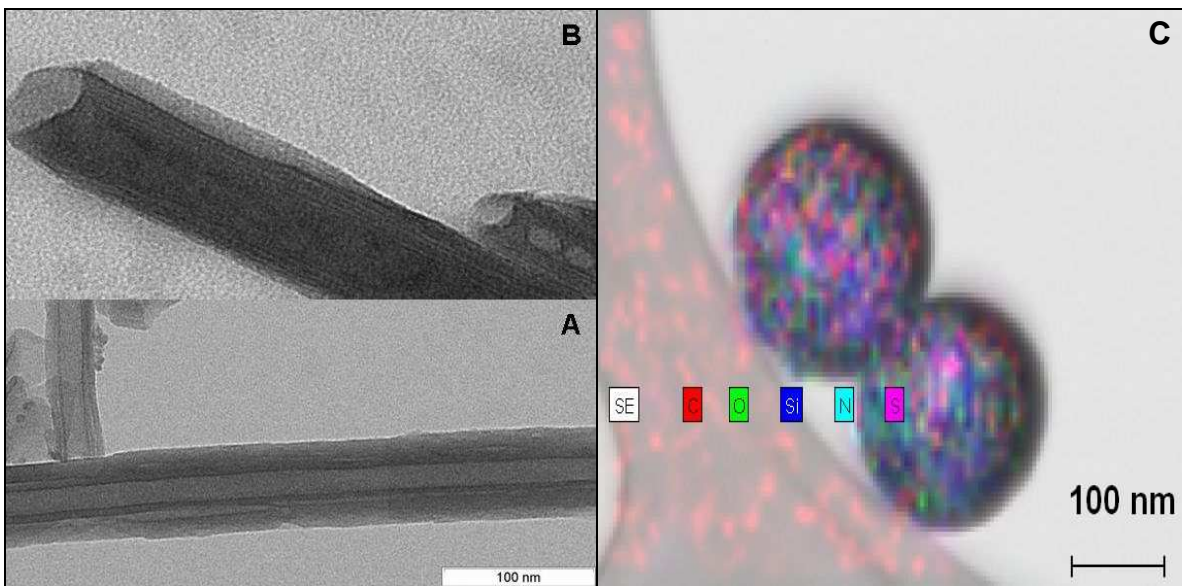
Figure 2. Mesoporous or hollow micro- and nanoparticles used for the preparation of containers ceramic core: A – halloysite nanotubes, scale bar below denotes 200 nm; B - spherical mesoporous silica (SMS) nanoparticles, scale bar denotes 100 nm; C - spherical hollow silica (SHS) nanoparticles, scale bar denotes 200 nm; D – mesoporous TiO<sub>2</sub> nanoparticles, scale bar below denotes 200 nm; E – commercially available silica microparticles, scale bar denotes 1 µm; F – commercially available aluminium modified silica submicroparticles, scale bar denotes 200 nm. For more details see text.

Halloysites are naturally occurring aluminosilicates with the average composition  $(Al_2Si_2O_5(OH)_4)_x n H_2O$ . Unlike other aluminosilicates such as kaolin etc., halloysite particles are tubuli-shaped (Fig. 2A) with the typical average dimensions of about 2 micrometer for the length and 50 nm and 15 nm for the outer and lumen diameters, respectively [17]. Tubular shape of these particles is believed to be caused by an irregular replacement of  $Al^{3+}$  by  $Fe^{3+}$  in the octahedral positions (3-10 wt % of  $Fe_2O_3$ ) due to geochemical processes in the Earth's crust [18].

Other class of naturally occurring clay based nanostructured microparticles used in the corrosion protective coatings is presented by layered double hydroxides (LDHs) which are also called as hydrotalcite-like substances [19]. Possessing brucite-like structure where some divalent cations were exchanged with various trivalent ones, LDHs compensate this excess of positive charge by intercalation of different guest anions between the host hydroxide layers. These anions may be replaced by different corrosion inhibiting anions like nitrates, chromates [20] etc. or even by anionic forms of organic inhibitors [19, 21] and then impregnated in the protective organic coatings. More simple method proposed recently is the targeted synthesis of LDH layers with inhibitor intercalation immediately in the vicinity of substrate under protection [22].

In contrast to the naturally originated halloysites, highly porous spherical silica nanoparticles were prepared by the surfactant templated polycondensation method. Morphology of particles, size and structure of pores depend on the type of template (micelles or emulsion droplets) and on the physicochemical conditions in the system determining the hydrolysis and polycondensation kinetics. In case of CTAB (cetyltrimethylammonium bromide) micelles in sodium hydroxide solution as template with the subsequent addition of TEOS (tetraethoxysilane), the hydrolysis and following gradual polycondensation of arising silanol molecules on the micellar template led to the so-called spherical

mesoporous silica (SMS) nanoparticles (Fig. 2B). These particles possess 2D hexagonally ordered cylindrical pores with the diameter of 3.5 nm and demonstrate very high values of specific area and pore volume, 1000 m<sup>2</sup>/g and 1 cm<sup>3</sup>/g, respectively. If however, TEOS and CTAB were initially mixed with water-ethanol solution and then the pH value of resulting emulsion was increased to 11.5 by addition of ammonia, the formation of spherical hollow silica (SHS) nanoparticles was observed (Fig. 2C). SHS particles do not demonstrate any structural order of pores but have a dense shell and a highly porous inner cavity. Their pore diameter, specific area and pore volume have however values equal or similar to these for SMS particles: 3.5 nm, 1000 m<sup>2</sup>/g and 0.9 cm<sup>3</sup>/g, correspondingly. Nanoparticles of mesoporous titania (TiO<sub>2</sub>) represent another example of artificially prepared ceramic nanoparticles. Heterophase oxidation of TiC powder by the concentrated nitric acid with subsequent multiple washing led (Fig. 2D) to the formation nanoparticles with average size of 400 nm and the moderate polydispersity (PDI = 0.35). The pore size distribution with the mean value of 10 nm as well as considerable total pore volume of about 0.35 cm<sup>3</sup>/g allowed the successful impregnation of these porous scaffolds by various inhibitors. Several sorts of mesoporous silica micro- and submicroparticles are commercially available for reasonable prices and can be directly employed for the fabrication of microcontainers for the following incorporation in coatings. So, figures 2E and 2F show two sorts of these particles, with the average sizes of 3.7 μm but very high total pore volume of 2.0 cm<sup>3</sup>/g as well as of 500 nm and 0.75 cm<sup>3</sup>/g, respectively.



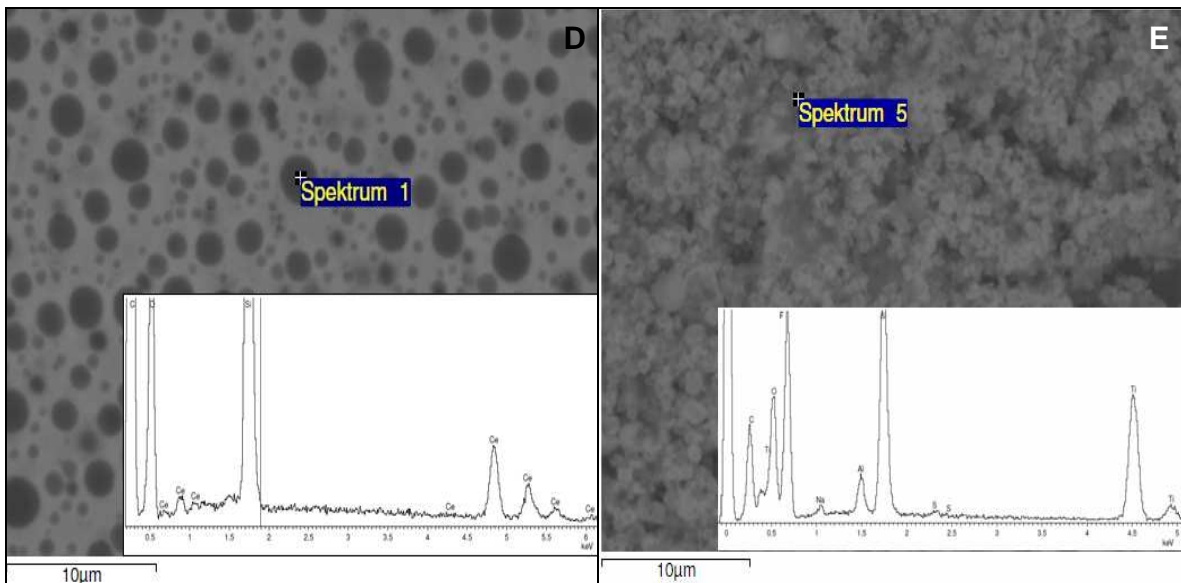


Figure 3. Ceramic container cores filled with inhibitors: A, B – empty halloysites and halloysites filled with ammonium molybdate, respectively; C – SHS silica particles filled with mercaptobenzothiazole (MBT); D – commercially available silica microparticles filled with cerium nitrate; E – commercially available aluminium modified silica microparticles filled with sodium hexafluorotitanate. For more details see text.

The second step in the container preparation consists of the impregnation of porous ceramic core with the chosen active agent or inhibitor. For this purpose, the ceramic particles are mixed with the concentrated solution of the inhibitor in an appropriate solvent (or pure inhibitor in the case of liquid inhibitors) and this mixture is then subjected to multiple vacuum cycles in a desiccator [5]. This procedure accelerates significantly the up-take of solution in the quite narrow pores normally sealed with the tiny gaseous stoppers (nanobubbles) and enhances finally the loading of the inhibitor. In addition, inhibitor molecules constrained in the confined volume of narrow pores become less mobile contributing as a consequence to the essentially extended release time for inhibitor impregnated into porous core and making therefore the release more sustained. Significant or complete wetting of particles material with the corresponding solution or liquid inhibitor is required precondition for the success of the impregnation step. Therefore, the proper selection of the solvent with the good wetting ability to the specific ceramic core and simultaneously excellent solvency for the chosen inhibitor are necessary for the high efficiency of containers loading. Usually, high loading values of ceramic mesoporous containers with the inorganic inhibitors are attained from their aqueous solutions whereas organic inhibitors are less water-soluble and can be essentially better loaded from organic solvents of intermediate polarity such as short-chain alcohols, ketones and esters. Some examples of inhibitor loaded hollow or mesoporous particles mentioned above are presented in figure 3.

The last step in the procedure of containers assembly is the creation of PE shell by Layer-by-Layer (L-b-L) alternate adsorption of opposite charged polyelectrolytes. The typical building blocks are such cationic polyelectrolytes as Poly(diallyldimethylammonium chloride), PDADAMAC; Polyallylamine hydrochloride (PAH); Polyethylene imine (PEI) and anionic ones like Poly(sodium 4-styrene sulfonate), PSS; Polyacrylic acid (PAA); Poly(methacrylic acid), PMA etc. but their combinations can vary depending on the specific properties desired for the future container shell. Figure 4 demonstrated schematically the process of containers build-up and its last step – the L-b-L PE deposition. Number of deposition and washing steps (in-between) depends on the desired thickness of the shell to be created and on requirements to its final composition. PE multilayers form envelop around loaded ceramic porous or hollow core of containers and decelerate significantly or almost stop the premature leakage



of the inhibitor from the container. Moreover, certain combination of polyelectrolytes can impart to the shell the special sensitivity to the changes in the local pH value making this factor to the specific trigger for the containers opening. The creation such pH-sensitive shells of micro- or nanocontainers can be achieved by deposition of weak cationic or anionic PE in alternation with strong oppositely charged PE. In the neutral pH range both polyelectrolytes are almost fully dissociated and attract each other electrostatically in the container shell. Charge compensation in the shell leads to its neutrality and quite high density especially in the dried state. Depending on the acidic or basic character of the weak PE, it becomes less dissociated in vicinity of either its pKa or pKb value, i.e. shift of pH value towards basic (for a weak cationic PE) or acidic (for a weak anionic PE) leads to the distortion of the charge compensation in the container shell and finally to its swelling due to electrostatic repulsion between individual layers. Because the onset and development of corrosion process is usually accompanied by local pH changes, the corresponding specific sensitivity of containers shell makes this effect of corrosion into trigger for the container opening and release of the encapsulated inhibitor. Finally, protective coating with such type of embedded containers demonstrates self-protecting anticorrosion functionality.

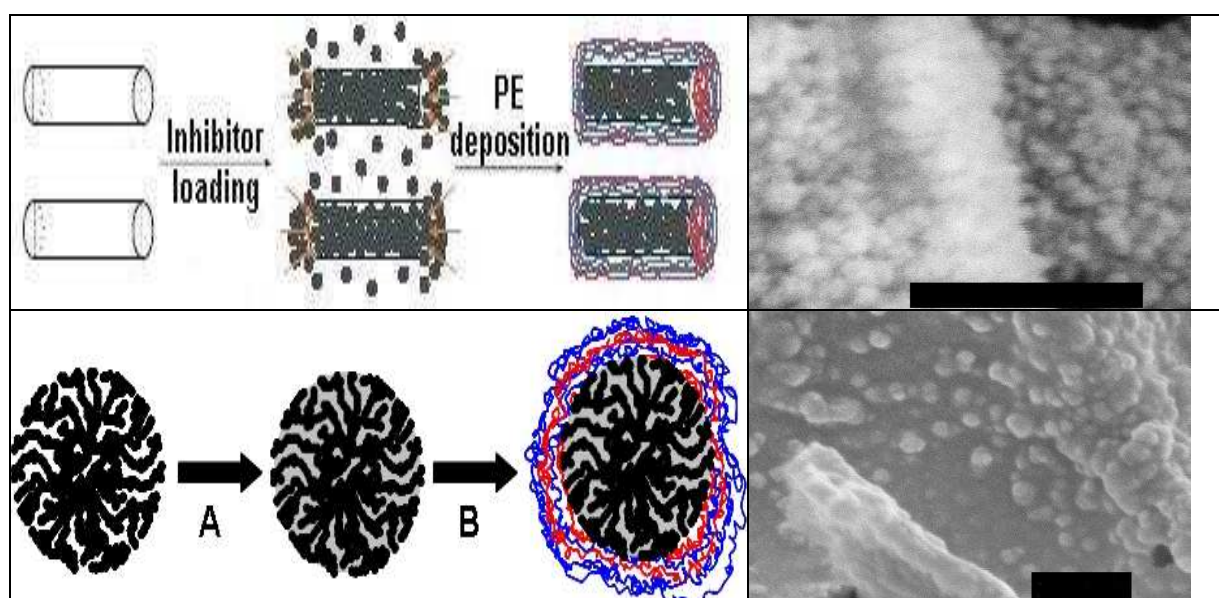


Figure 4. Schema of assembly steps at the preparation of ceramic particle based nano- or microcontainers. The second step on the left top and bottom pictures represents the L-b-L alternate PE adsorption halloysite nanotubes and mesoporous ceramic particles, respectively. Microphotographs on the right show the surface of mesoporous ceramic particle before (top) and after (bottom) deposition of PE multilayer, scale bars denote in both cases 200 nm.

## B. Polymeric and composite containers prepared on the basis of direct or inverse emulsions

As it was shown in the previous paragraph, containers assembly procedure involving the use of ceramic hollow or mesoporous micro- or nanoparticle as scaffold and container core is a multistep process. Loading capacity and the number of loading steps depend on the scaffold porosity as well as pores size distribution and can be additionally complicated in the case of narrow pores. Together with at least two-step deposition of PE shells of containers, this makes the entire fabrication of this containers type not always simply and economically sound enough.

In contrast, the use of emulsion as an initial point for the preparation of micro- or nanocontainers demonstrates several advantages over the above mentioned approach employing the ceramic

particulate cores. First, the emulsion based method is the straightforward one, the simultaneous two-fold role of emulsion droplets – as templates and as containers cores allows the significant reduction of steps at the containers assembly. The initial liquid state of both phases decreases substantially the comminution work needed for the preparation of the colloidal system especially by use of surfactants. The liquid state of the containers cores enables the precise control for concentrations of all ingredients and provides on the one hand the fine adjustment of the active agent content and its distribution in the container and, on the other hand, the flexible regulation of containers size distribution. Direct encapsulation of emulsions becomes especially important when the formation of containers with core/shell morphology and a liquid core is desired. This situation may for instance be of especial importance when in case of destructive external impact the strong immediate feedback of the protective coating is required.

Starting point for the preparation of all specific types of emulsion based containers is the fabrication of “direct” oil-in-water (O/W) or “inverse” water-in-oil (W/O) emulsion. The liquid/liquid interface between the droplets of dispersed phase of emulsion and its continuous phase serves then as the “scene” where the formation of the container shell proceeds. Vast majority of containers obtainable by the emulsion route can be roughly divided in two wide groups, depending on the nature of the event leading to the formation of the container shell: containers for which preparation the physical phenomena are exploited and, containers whose underlying processes are of the chemical nature.

## **B I. Containers formed by means of interfacial physical phenomena**

### **A. Containers prepared by the use of solvent induced interfacial precipitation**

At the preparation of containers by this method, the emulsion droplets function as soft template particles at whose interface the shell-forming material begins to precipitate due to changes in its concentration. Moreover, the same droplets contain the substance to be loaded into containers and serve therefore as their future cores. The shell-building component is initially fully dissolved in the droplets of dispersed phase (emulsion droplets) so that both phases of this disperse system (emulsion) remain at the beginning homogeneous. Upon the changes in the concentration of solvent with the good solvency for the shell-forming substance occurring in the system, its solubility in the drops is decreased and it starts to precipitate.

Generally, the decrease of the solubility of the shell-forming compound in the emulsion droplets with subsequent precipitation at their interface can be induced by changes in the composition of the dispersed phase – either by removal of the solvent having a good solvency for this compound or by addition of the solvent possessing a poor solvency for it (“non-solvent”). Since the dispersed phase is non-autonomous one, all changes in its composition are mediated by the corresponding changes in the dispersion medium. Typical processes leading to the interfacial precipitation are evaporation of the solvent from this phase or its dilution by the non-solvent, i.e. solvent evaporation induced precipitation or dilution induced precipitation.

Micro- and nanocontainers for the self-protecting anticorrosion coating containing the water-repelling agent sodium docusate (AOT) were prepared in our group [23] by application of the solvent evaporation induced interfacial precipitation technique to the O/W emulsion. The droplets of dispersed oil phase were composed of AOT, solvent for it (dodecane), volatile co-solvent sparingly soluble in water (ethyl acetate, EA) and polystyrene (PS) as shell-forming component. This emulsion stabilized by the appropriate surfactant was left for the EA evaporation under the fume hood with continuous stirring at 150 rpm for 12 hours or, to accelerate the removal of this solvent, firstly diluted ten times with Milli-Q water and then treated by the dry nitrogen bubbling for 5 hours. Volatile EA was completely evaporated and an aqueous dispersion of PS micro- and nanocontainers containing a solution of AOT in dodecane was obtained. Interestingly that the containers obtained only by the gradual evaporation of EA without acceleration showed lower polydispersity probably because of the Ostwald ripening in the initial emulsion droplet that kept in this case their liquid state longer.

In spite of simplicity and relatively low costs of interfacial precipitation method in its various concrete realizations there is also a lot of challenges and drawbacks connected with some technical peculiarities of this method and with the properties of containers obtained in this manner related to their embedding into coating matrix. Solvents used for the dissolution of shell-forming component(s) have to be either completely or at least sparingly soluble in the dispersion medium, most often aqueous one. These solvents should be also volatile enough to assure a reasonable time of complete evaporation and formation of the container shell. Therefore, the application of this method in both solvent evaporation induced precipitation and dilution induced precipitation types will lead to the serious amounts of environmentally dangerous wastes such as volatile organic compounds (VOCs) or VOCs-contaminated water especially when up-scaled to the industrial extent. Because of these environmental concerns the industrial realization of interfacial precipitation method may be additionally complicated by the necessity to install quite expensive recycling set-ups.

Another problem is that polymers used for the formation of containers shell are the preformed polymers, which should be well-soluble in several solvents of intermediate polarity ensuring the good miscibility with both aqueous and oily phases. Thus, the relatively low cross-linking degree of polymers employable for this purpose is required. On the other hand, the high solubility of shell-forming polymers in the solvents of moderate polarity excludes automatically the incorporation of containers made of these polymers in the coatings that are formulated by use of organic solvents and restricts their use only to water-born coating formulations. But even in this case, the coating formulations with relatively high curing temperature can be also subject of doubt since the low cross-linking degree of polymer will cause its melting already on the curing step with subsequent destruction of containers.

#### B. Containers prepared by means of Layer-by-Layer (L-b-L) PE interfacial adsorption

Universal approach to the preparation of loaded micro- and nanocontainers based on the direct emulsion encapsulation by PE L-b-L adsorption was developed only recently [24]. In this method, the liquid colloidal particles (O/W emulsion droplets) were made of water-immiscible solvent (dodecane). To stabilize the dispersed phase of initial emulsion and to ensure the significant interfacial charge of droplets for the beginning of PE deposition, the oil phase was doped by small amount of cationic surface-active precursor Dioctadecyldimethylammonium bromide (DODAB). Because of its very low solubility in nonpolar solvents, 30 v/v% of chloroform was added to dodecane in order to improve the precursor solubility in the oil phase. The droplets of O/W emulsion however did not contain any detectable traces of chloroform during the PE deposition steps since its considerable solubility in the aqueous media. Colloidal stability of initial emulsion was achieved due to concentrated monolayer of strongly positively charged DODAB (Zeta-potential was about +90 mV) at the surface of each droplet. The L-b-L polyelectrolyte assembly was done by their subsequent adsorption from concentrated (20 mg/ml) aqueous salt-free solutions. The creamed upper layer of the strongly positively charged initial emulsion was added dropwise to the oppositely charged solution of PSS upon continuous stirring ensuring the overcharging of droplets interface. The excess of the remaining free polyelectrolyte was washed out by pure MilliQ water. The second encapsulation step was done in an aqueous solution of cationic PE PDADMAC or PAH in the same manner. The further repetition of the alternating adsorption steps leads to the formation of containers with desired shell thickness depending on the particular final demand. Resulting containers had Z-average size of 4.2  $\mu\text{m}$  and were quite monodisperse (PDI = 0.32). The dried droplets of O/W emulsion encapsulated by L-b-L interfacial adsorption technique are presented in the figure 5A. Since the procedure of drying leads in the case of PE oil-filled containers to their collapse especially on the steps connected with the preparation of SEM samples, the oily containers cores can not be kept intact and only wrinkled PE containers shells are observable (Fig. 5) supporting the PE multilayered shell assembly around O/W emulsion droplets.

Following the proposed paradigm for the straightforward preparation of the emulsion-based PE containers [24] further progress in this field was achieved [25, 26]. Wackerbarth *et al.* [25] reported PE microcontainers on the emulsion basis with six layers of biopolyelectrolytes for the potential application

in the food industry. The authors of ref. [26] have presented the successful PE encapsulation of highly unstable polyunsaturated natural oils for the aims of storage and degradation protection by introducing the natural antioxidant compound (tannic acid) as shell constituent in alternation with biocompatible oppositely charged polyelectrolyte.

Container prepared via PE L-b-L direct emulsion encapsulation technique can be envisaged as quite applicable in several types of protective coatings, especially water based, imparting to them some unique functionalities independently of the nature of components encapsulated in the core. This can be achieved due to the many polyelectrolytes available for L-b-L container shell assembly. Purposeful choice of PEs for the containers shells allows their opening by numerous environmental or artificially introduced triggers such as temperature [27], pressure [28], changes in pH [29], ionic strength, electrochemical potential etc. and therefore enables the specific stimuli-responsive protective ability of coatings carrying these containers.

Nanometric accuracy provided by PE L-b-L deposition on the each step of the container build-up allows very fine adjustment of their size and the shell thickness that also can be of high practical importance in many research and industrial fields.

On the other hand, some drawbacks of PE containers obtained by the L-b-L interfacial adsorption should be also mentioned here making their utilization in many types of self protecting coatings problematic. Even at deposition of PEs with lowest  $M_w$  the permeability of shell for low-molecular agents loaded into containers remains high disabling the possibility of sustained release for these substances and use of such type of containers in the media with good solvency for the core material. Low mechanical stability of the PE shells at any reasonable number of PE layers in the shell is the other source of trouble. It can be significantly improved by the increase of L-b-L deposition steps and subsequent annealing at higher temperature [27] but such an overcomplicating makes the fabrication costs rising and thus unacceptable for many potential application fields. At the same time, the use of soft emulsion based containers with L-b-L PE shells is imaginable in the water-born coating formulations with the quite mild curing conditions and ductile coating matrices.

### C. Containers on the basis of Pickering emulsions

This method of preparation of emulsion-based nano- and microcontainers relies on the remarkable phenomenon of emulsion stabilization by the partially hydrophobic/hydrophilic micro- or nanoparticles due to their spontaneous attachment at the O/W or W/O interface, respectively. This particle behaviour can be strictly described in terms of change in the particle energy upon its transition from the bulk location to the interface [30]:

$$\Delta G_{att} = -\pi r^2 \gamma_{\alpha\beta} (1 \pm \cos \theta)^2 \quad (7)$$

Thermodynamically, this transition can be considered as practically irreversible even in the case of small nanoparticles and is therefore called commonly not as “adsorption” but as “attachment”. Due to these reasons, the partially hydrophobic/hydrophilic particles form spontaneously a tight mono- or even multilayer at the emulsion droplets interface acting as building blocks for the containers shells. Again, the emulsion droplets serve as template for the formation of the particulate shells and work at the same time as reservoirs for the loaded active agent.

The interfacial activity of particles can be an intrinsic property of them connected with their specific affinity to certain types of solvents. In this case even the bare unmodified particles are able to concentrate at the interface between droplets of this solvent and surrounding medium [31]. Much more frequently however, this peculiarity is imparted to the particle by its surface modification using various types of surfactants [32 – 34] bonded electrostatically or covalently to the particle material. Electrostatic

mechanism of the modification does not presume the formation of the proper chemical bonds between surfactant molecules and particle surface but is rather a result of the equilibration of the complex physical interactions between these molecules, particles and surrounding medium (solution). Therefore, the small amounts of free surfactant molecules always persisting in the system can occasionally interfere with the corrosion inhibitor or other protective agents in the core-forming emulsion droplets and impair the mechanism of the interfacial particle attachment. To avoid this undesired situation, the thorough selection of appropriate non-reacting and non-interacting surfactants and protective components should be done before fabrication of containers. The indicated problem will however not arise at all when inhibitor molecules possess by themselves the certain surface activity and can therefore simultaneously cause the partial hydrophobic modification of the particle surface. Many corrosion inhibitors are weak organic acids, bases or amphoteric compounds having functional groups partially or fully ionized in a certain pH range and therefore becoming hydrophilic. In case when the residual organic moieties of inhibitor molecule are hydrophobic enough the entire molecule will demonstrate the amphiphilic behaviour in the same pH range, i.e. will act as a surfactant. We utilized the corresponding ability of the amphoteric corrosion inhibitor 8-hydroxyquinoline (8-HQ) [35] to become considerably protonated at the pH less than 5.5 ( $pK_a = 5.13$ ) and to be adsorbed electrostatically on the surface of negatively charged silica nanoparticles (Ludox TMA) in order to make them partially hydrophobized and therefore interfacially active. These particles stabilize the O/W emulsion droplets forming the multilayers at their interface that can be considered as particulate containers shells. The droplets of dispersed phase are composed of Diethyl phthalate (DEP) with dissolved 8-HQ and serve as containers cores and reservoirs for the loaded inhibitor. The containers size distribution and the amount of nanoparticles in the containers shells were well-expressed functions of pH in the range from approximately 4.4 till 5.6. At pH 4.4 the monodisperse containers with volumetric average size of 4.5  $\mu\text{m}$  and PDI of about 0.4 were obtained. This pH-dependent behaviour can be related to the continuously increased interfacial activity of silica nanoparticles hydrophobized by the gradually growing amount of the adsorbed 8-HQ upon pH drop. Below the pH 4.4, protonation degree of 8-HQ and subsequently its concentration in the dispersion medium attain the values enabling the formation of an 8-HQ bilayer on the surface of silica nanoparticles. The interaction of the overlapping aromatic rings, could be suggested as a driving force for this effect. As a result, the positively charged protonated groups of 8-HQ molecules in the outer part of bilayer are oriented towards dispersion medium and re-hydrophilize the particles in the containers shells. The rapid destruction of the containers is observed in this pH region leading to the immediate burst-like release of the encapsulated inhibitor. This pH-sensitivity as well as the mechanical rupture of containers could be utilized as triggers for the containers opening and stimulated inhibitor release when the containers become embedded in the matrix of a self-protecting anticorrosion coating.

Emulsion based containers fabricated by means of interfacial attachment of nano- or microparticulate building blocks forming the container shell reveal several advantages in the preparation routine and in the following handling fashioning them as potential candidates for the use in the various self protecting coatings. Fabrication of micro- and nanocontainers by means of interfacial attachment method is usually quite simple procedure that includes as a rule only two steps – (i) preparation of particles as building blocks for the shells of future containers due to their partial hydrophobization (O/W) or hydrophilization (W/O), and (ii) addition of them to the two-phase system containing all components of containers during or immediately before the emulsification with subsequent processing leading to the ready containers. Sometimes this procedure can be even further simplified to the practically one-pot process [31]. Due to its simplicity, this preparation pathway may often be economically sound and has a high practical relevance. Wide variety of particles of different chemical nature and of immiscible solvents with diverse polarities available facilitates an almost unlimited number of achievable containers types thus making the method very comprehensive. Comparing with the types of the emulsion-based containers described above, containers prepared by the interfacial attachment of particles demonstrate much higher robustness [36] and are therefore more suitable for the incorporation into self protecting coatings with hard coating matrices. However, the main problem in the application of containers



prepared by interfacial attachment remains the heterogeneity of their shells comprised of many fine particles joined at the surface of each emulsion droplet to a mono- or multilayer with the lot of gaps between individual building blocks. This discontinuous structure of the container shell reduces considerably its mechanical properties especially comparing with these of the individual particle in the shell and increases its permeability drastically. The latter could be very critical when the containers loaded with the oil-soluble protective agent are mixed with a solvent based coating formulation able to wash out the containers load immediately after their addition into coating mixture.

To enhance the mechanical strength of containers and make them more seamless, single particulate elements of the containers shells should be locked at the interface and joined together. It can be done for instance by the local high energy treatment as was shown in Ref. [37] where the high intensity ultrasound was used for this purpose. The second possibility is the interlinkage of particles in the shell by the deposition of additional PE layers atop it. This, on the one hand, complicates the process of the containers preparation by one more step but on the other hand can significantly improve the integrity and permeability of their shells. Moreover, the PE deposition could impart to shells certain additional valuable features connected with the properties of polyelectrolyte layer like selective pH sensitivity etc. Figure 5B shows containers on the basis of Pickering emulsion droplets made of 1.5 M solution of 8-HQ in dimethyl phthalate (DMP) coated with 3 PE bilayers composed of pairs PAH/PSS or PAH/PAA. Alternate deposition of polyelectrolytes not only did not disturb the initial containers size distribution with volume average size of 2.5  $\mu\text{m}$  and PDI =0.35 but also led to the significantly higher stability of containers that remained almost not deformed during the SEM sample preparation.

## **B II. Containers prepared by the interfacial or bulk chemical reactions in emulsion droplets**

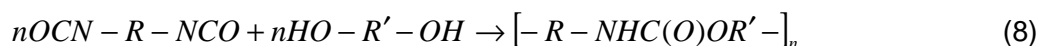
Containers formed in the course of a chemical reaction proceeding either at the emulsion droplets interface or in the droplets interior can be considered as another class of containers which in turn may be further subdivided in two big groups: containers prepared using the interfacial polyaddition or polycondensation reaction and containers obtained by in-situ emulsion polymerization taking place in the bulk of emulsion droplets.

### **A. Containers via Interfacial polyaddition/interfacial polycondensation**

At the containers synthesis by interfacial reaction in an emulsion, at least one of reactants is distributed outside droplets in the continuous phase of emulsion whereas the other are dissolved in the droplets. Usually it is achieved by use of reactants of different polarities that are predominantly soluble only in one of coexisting phases, either in continuous or in dispersed one. In this manner, one can prevent the interpenetration of dispersed reactants in the coexisting phases and premature reaction between them. Moreover, reactants have to remain phase-separated all the time when reaction goes on and meet each other only at the interface of emulsion droplets where the reaction between them occurs. If the product of such an interfacial reaction is insoluble in both coexisting phases, containers become the core/shell morphology. In more probably opposite case when the arising product is soluble or swellable in the material of dispersed phase, particles with the solid bulk structure occur [38].

The encapsulation of the mixture of protective agents with two functionalities – corrosion inhibitors and simultaneously water repellents – was performed recently [39] by the interfacial polyaddition technique for the further application in the self protecting anticorrosion coatings. The oil phase of the O/W emulsion was composed of mixture of two protective agents, trimethoxy(octadecyl)silane (TMODS) and trimethoxy(octyl)silane (TMOS), trifunctional pre-polymer Poly[(phenyl isocyanate)-co-formaldehyde] participating in the reaction of shell formation as well as solvent (DEP) enabling the miscibility of all components. This mixture was dispersed in an aqueous medium by means of non-ionic polymeric emulsifier polyvinyl alcohol (PVA) under intensive stirring with high speed rotor-stator homogenizer.

Resulting emulsion was added to the phosphate buffer solution containing the second water-soluble reactant glycerol and polyaddition reaction catalyst 1,4-diazabicyclo[2.2.2]octane (DABCO). The formation of polyurethane (PU) containers shells at the interfaces of droplets was occurred according to the following reaction scheme:



This mixture was left for 1 hour at 65°C under stirring and subsequently overnight without heating and stirring for the completion of containers formation. Finally, quite polydisperse microcontainers with the well-expressed core/shell morphology (Fig. 5C) were isolated. The size distribution of PU containers demonstrated two peaks representing two main fractions of containers in the mixture – one at 1.0 µm and the second one – at 5.5 µm. At the increasing of rate of the high speed rotor-stator homogenizer from 11000 rpm through 16000 rpm to 22000 rpm, the area of the first peak was continuously increased with the subsequent reduction of the second one remaining however still bimodal. Such a bimodal particle size distribution can be considered as polymerized replica of an initial O/W emulsion predestined by its droplets size distribution [40] almost always showing a high polydispersity if the high speed rotor-stator homogenizer was applied for the emulsification process. Utilization of ultrasound for this purpose leads as a rule to narrower and frequently monomodal droplet size distribution in the original emulsion [41]. Application of this comminution method in the considered case of containers with PU shells was unfortunately impossible because of numerous sonochemical effects accompanying the collapse of cavitation bubbles upon ultrasound propagation. Reactive isocyanate functional groups in the pre-polymer molecules quickly underwent side reaction with water molecules and highly reactive products of the water thermolysis (free radicals, hydroxyl-carrying species etc).

Figures 5D & 5E demonstrate other example of containers obtained by the interfacial polycondensation technique. The containers presented here have silica shells and are filled with the corrosion inhibitor mercaptobenzothiazole (MBT) dissolved in the organic solvent dibenzyl ester. These two compounds along with the shell-forming component TEOS were mixed together to form the oil phase of the future emulsion. Oil phase was dispersed in an aqueous phase with pH = 11.5 using the cationic surfactant CTAB and the resulting emulsion was then left over night at 65 °C. Formation of container shell made of silica was achieved due to gradual hydrolysis of TEOS with the silanols as semi-products and their subsequent condensation on the surface of liquid colloidal template. At the end, the polydisperse submicrocontainers (Zeta average size 700 nm, PDI = 0.43) filled with inhibitor MBT (see EDX spectrum in the figure 5E) were collected.

These containers can be successfully applied in the anticorrosive self healing and self protecting coatings in cases when the corrosion is caused or followed by the pH increase. The dissolution or of silica shell in this pH range can lead to the corrosion-triggered release of inhibitor.

Containers filled with many other corrosion inhibitors and biocides and shells made not only of polyurethane but also polyurea (PUa) and polyepoxy resins were as well synthesized by the interfacial polyaddition method. The two latter polymers are especially suitable as container shell materials since both of them are sensitive to the reduction of pH to low or middle-low values, i.e. the release of protective agents can be triggered by this factor accompanying corrosion and stop the further development of the process.

### B. Containers via *in-situ* emulsion polymerisation

Realization of this containers preparation technique presumes that all reactants needed for the synthesis are already from the beginning contained in the emulsion droplets. These play now the two-fold role of reservoirs for reactants and protective agents as well as of liquid colloidal reactors and are only kinetically stabilized against the start of the premature reaction. After the O/W or W/O emulsion with desired properties such as stability, concentration, droplet size distribution etc. is prepared, the

chemical (initiator substance, catalyst) or physical (T, UV-light etc.) triggers are activated to switch on the reaction and it runs until the attainment of the real equilibrium state corresponding to the completion of the polymerization reaction.

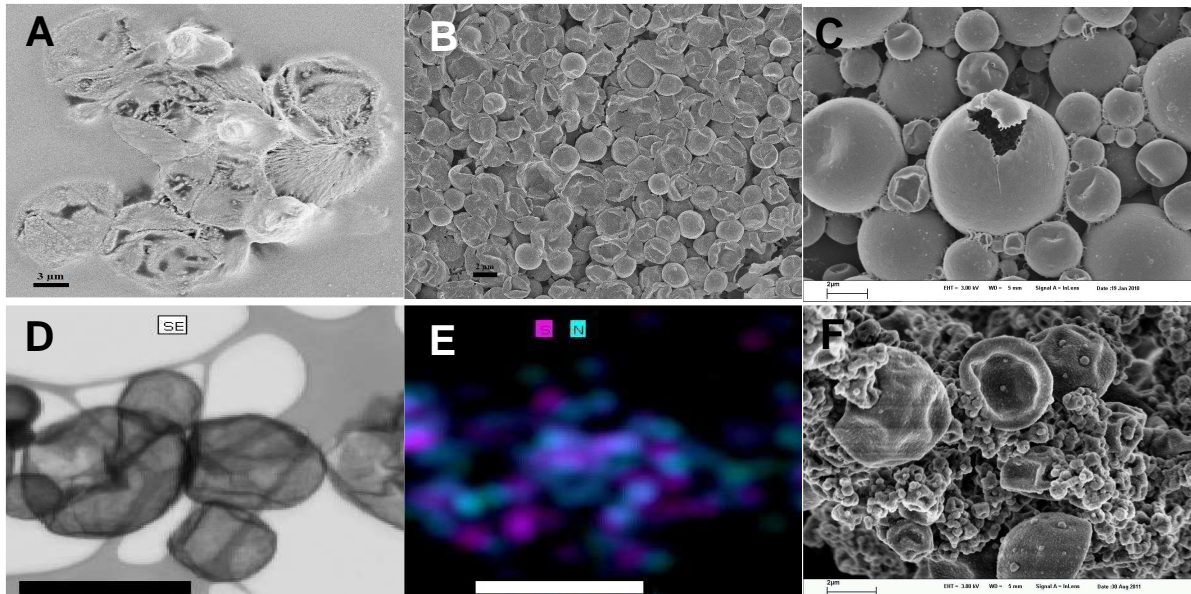


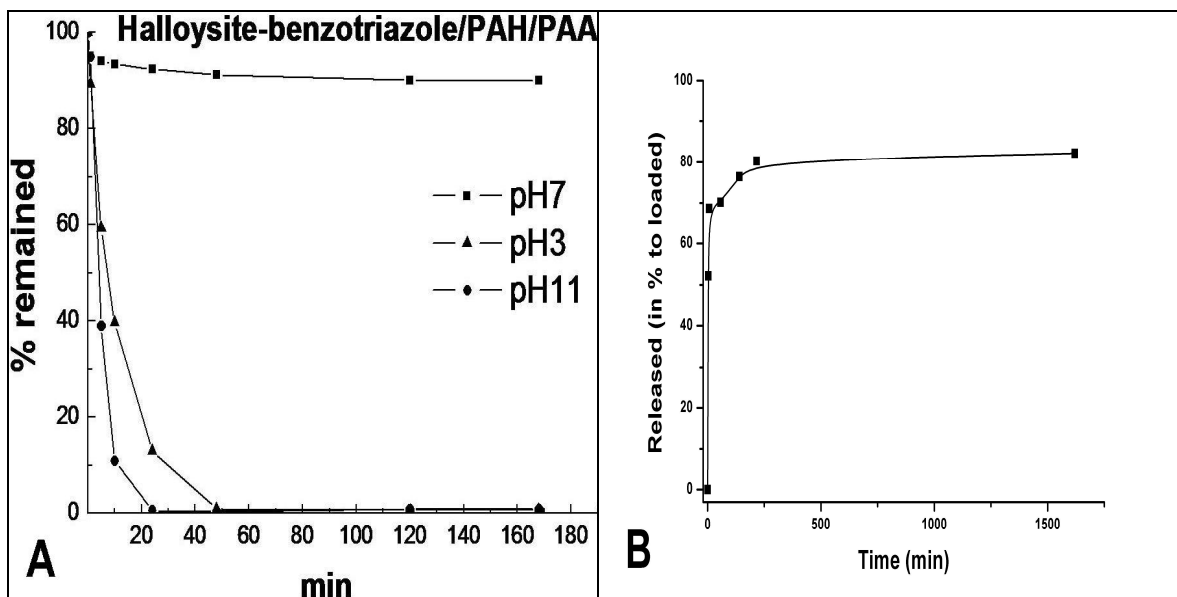
Figure 5. Micro- and nanocontainers obtained by use of different chemical and physical interfacial phenomena: A – containers from droplets of O/W emulsion prepared by PE L-b-L interfacial adsorption technique [24], scale bar below denotes 3  $\mu\text{m}$ ; B – containers on the basis of Pickering emulsion with subsequent particles locking by PE L-b-L interfacial deposition [23], scale bar denotes 2  $\mu\text{m}$ ; C – Microcontainers with Polyurethane (PU) shells loaded with the siloxanes mixture prepared by interfacial polyaddition reaction [39], scale bar denotes 2  $\mu\text{m}$ ; D & E – Nanocontainers with silica shell loaded with corrosion inhibitor mercaptobenzothiazole, TEM and EDX pictures, scale bar denotes 1  $\mu\text{m}$ ; F – Polyepoxy micro- and nanocontainers filled with the corrosion inhibitor methylbenzothiazole (Me-BT) obtained by *in-situ* polymerization of O/W emulsion [23], scale bar denotes 2  $\mu\text{m}$ .

The polyepoxy containers filled with the corrosion inhibitor methylbenzothiazole (Me-BT) for the self protecting anticorrosion coatings for aluminium substrates were prepared by *in-situ* polymerization method [23] by the following steps. The mixture of reactants needed for the formation of polyepoxy shells of containers was initially prepared composed of the 1:1 combination of aromatic and aliphatic epoxy-monomers trimethylolpropane triglycidyl ether and tris(4-hydroxyphenyl)methane triglycidyl ether, respectively. 20 % of Me-BT related to the total mass of the mixture was then added. The final step in the preparation of oil phase of the future emulsion was the addition of the second reactant for the *in-situ* polymerization reaction – diethylenetriamine in the amount ensuring the slight excess of the stoichiometric equivalence with the sum of both epoxy components. The oil phase was dispersed in the 2 wt% aqueous solution of the non-ionic emulsifier PVA using a rotor-stator high speed homogenizer. The dispersion medium of the O/W emulsion obtained was then doped with a small amount of polymerization catalyst tetrabutylphosphonium bromide to increase the reaction rate to a reasonable level. The mixture was left overnight under moderate stirring to complete the polymer formation. The resulting containers are very polydisperse (see Figure 5F) with the volume-average size of 2.3  $\mu\text{m}$  (PDI = 0.96) and have obviously the core/shell morphology. This containers structure reveals the phase separation within emulsion droplets in the course of the polymerization reaction leading finally to the segregation of core and shell parts of containers. Again, the significant improvement of the containers size distribution by the creation of the more monodisperse initial O/W emulsion via ultrasonication was not possible because of the immediate reaction of epoxy-monomers with water and especially with the

products of sonochemical processes. Due to presence of free amino-groups in the structure of the obtained epoxy polymer, the containers showed high positive surface charge (Zeta-potential of about +45 mV) and were therefore well-dispersible in various aqueous media, for instance, in the water based liquid coating formulations. Moreover, the introducing of epoxy monomers with the functional groups easily hydrolysable in the acidic or basic surrounding (like ester-groups) allowed their opening in these media and finally acid- or base-triggered release of protective agents from the containers.

### Release of encapsulated active agents from nano- and microcontainers

Kinetics of release of an encapsulated corrosion inhibitor or other active agent is very important characteristic of containers strongly affecting the rate and intensity of protective feedback of the coating in which these containers are incorporated. Of course, there are some other factors that can also influence the feedback kinetics like distribution of containers in the coating matrix, its permeability for molecules of encapsulated agent as well as for the molecules of surrounding medium etc. but the release properties of containers themselves remain the main parameters that determine their selection for the particular practical application. Basically, shell thickness and indirectly related to it permeability foreordain the release from container. Both these parameters can be widely varied at the containers assembly. The precisely controlled thickness of containers shells can be designed by the exact components ratio during the synthesis of polymeric containers either via interfacial or via in-situ polymerization methods. In case of containers with the porous ceramic core and PE shell, even the nanometric accuracy is possible through the number of individual steps of alternate polyelectrolytes deposition.



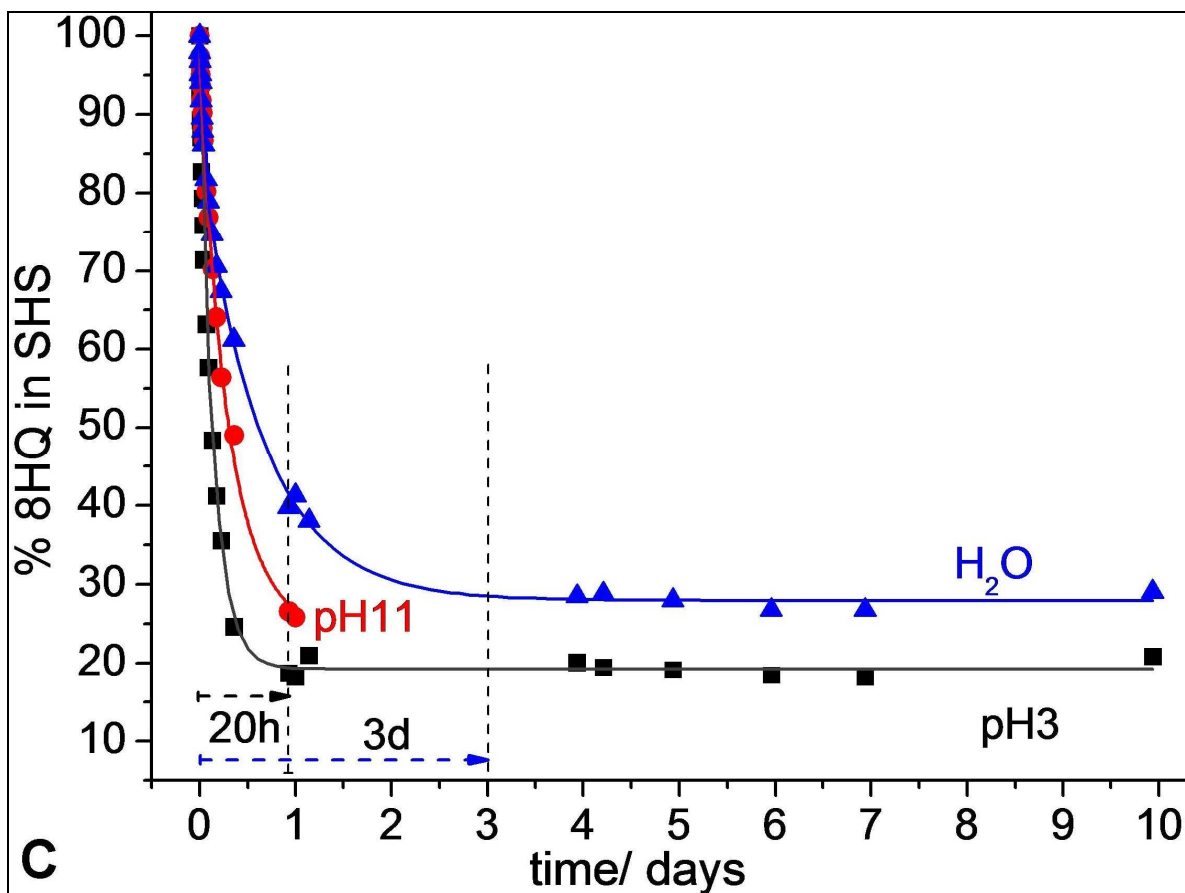


Figure 6. Release kinetics from containers freely distributed in media: A – Halloysite based containers enveloped in PE shell loaded with benzotriazole at different pH in the aqueous medium; B – containers with polyurethane shells loaded with biocide 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT) in ethanol medium; C – SHS silica containers loaded with inhibitor 8-Hydroxyquinoline (8-HQ) at different pH in the aqueous medium.

Along with absolute thickness of the container shell, the chemical nature of the shell material is crucial for the kinetics of release especially in relation to the active agent encapsulated and to the medium where container should be then dispersed. If the product of interfacial or bulk polymerization reaction is swellable in the containers cores due to good solvency of liquid inhibitor or auxiliary co-solvent used for the homogenization of oil phase prior emulsification step, the resulting containers do not acquire the core/shell morphology but are rather compact gel-like particles [38] revealing slow and sustained release of the encapsulated substance. Solubility or swellability of shell-forming material should be also taken into account on all steps of containers incorporation in the final coating. Containers have to remain stable already on the stage of their mixing with the coating formulation (free-standing containers) and then during the subsequent application and curing steps until their exposure to the aggressive surrounding (containers embedded in the coating matrix). To prove the influence of certain components of the coating formulation where the containers should be distributed before the application step, the release from the containers freely dispersed in the medium mimicking this solvent mixture has to be studied. For instance, the containers with ceramic cores and PE shells are suitable predominantly for the use in aqueous coating formulations because of the polar character of their shells. In order to check the influence of these media on the shell properties and therefore on the release behavior of containers they were incubated in buffer solutions with different pH values and the corresponding release kinetics were investigated. The results of this study are given in Figure 6A

showing fast and almost complete release of active agent (corrosion inhibitor benzotriazole) in acidic and basic pH ranges. These findings are consistent with the strong swelling of PE complexes made of two weak polyelectrolytes – basic PAH and acidic PAA in the same pH windows. Swelling of PE shells of containers is therefore responsible for the opening of containers and release of inhibitor at low and high pH values which can be used as triggers for the protective feedback activity of coatings containing this sort of containers.

On the contrary, Figure 6B shows the example when the medium impact on the containers shells leads to the quick release of the encapsulated active agent. Burst-like release of the biocide 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT) from PU microcontainers in an ethanol medium demonstrates clearly that this type of containers is completely inappropriate for use in the coating formulations with the media of similar polarity and solvency as ethanol.

For containers with porous or hollow ceramic core, the shape of hollow lumen and pore size distribution are additional factors that contribute significantly to the final rate of release. Figure 6C demonstrates that in case of especially high porosity of the core and very fine pores (containers made on the basis of SHS silica nanoparticles), the release of the loaded substance from the core may last a considerable time. Changes in the pH value of the surrounding medium affect the release kinetics additionally because of the corresponding changes in the surface charge of the ceramic core and amphoteric character of the loaded inhibitor 8HQ.

Combination of containers providing both fast and continuous slow release in the same coating matrix seems to be especially suitable for an optimal protective performance of this coating. Initial strong burst-like release at the site of the damage ensures the high local concentration of inhibitor or other protective agent leading to the immediate creation of its protective layer on the metal surface whereas the following gradual release of small portions of inhibitor over long-term period provides the sustainability of the protection.

### **Distribution of micro- and nanocontainers in the matrices of novel container based protective coatings**

Distribution of containers in the coating matrix is another very important parameter that can strongly influence not only the stimuli-responsive ability of novel coatings but also affect their barrier properties. Conventionally, the proper size of containers for the incorporation in a coating is suggested to be optimal if they have the size of about 10% of the total coating thickness. This ratio between coating and containers dimensions ensures the maintenance of the coating integrity also after incorporation of containers including the most critical situation when some small aggregates of containers will be formed during some steps of the coating build-up. However, even in almost ideal case of small and non-aggregated containers, the formation of local areas with the enhanced concentration of containers within coating matrix may lead to the deterioration of barrier properties of this coating and subsequently to the failure of its anticorrosion performance [42]. Moreover, location of containers predominantly in a certain part of the coating matrix can also influence the response rate of novel coating to the damaging impacts. As it was shown very recently [43], increasing the distance between containers localization and metal surface to be protected led to better barrier properties but worsened the active corrosion inhibition. The opposite situation when containers are located close to the substrate caused the decrease of passive protection of the coating.

Distribution of containers in the matrix of the cured coating is closely related to their dispersibility in the initial coating formulation. This characteristic, in turn depends on the interplay between the interaction of containers with themselves (cohesion) and with solvent components of the coating formulation (adhesion). If the work of adhesion exceeds the work of cohesion the wetting of containers by the coating formulation medium is energetically disadvantageous and they tend to form aggregates. In favorable case of lower adhesion work, the good wetting of containers is achieved and they may be dispersed well in the coating formulation. Other important preconditions for stability of containers dispersion are electrostatic or steric barriers around containers preventing their aggregation. On the



other hand, such factors as high density difference between material of containers and the formulation medium as well as presence of other particles (in worst case – of opposite charge) such as particles of the color pigment etc. can lead to the destabilization of containers dispersion in the liquid state of coating formulation and then to their inhomogeneous distribution in the matrix of the cured coating. Creation of electrostatic or steric barriers protecting containers from the premature aggregation can be performed by means of their surface modification. Most frequently, substances having the surface activity are used for this purpose including ionic, non-ionic and polymeric surfactants. Modification of containers surface by surfactants can also essentially improve their wettability by the formulation medium providing their better dispersibility in this formulation. In this manner, the stable dispersions of quite polar containers may be prepared not only in polar (aqueous) media but also in the media with much higher hydrophobicity [44].

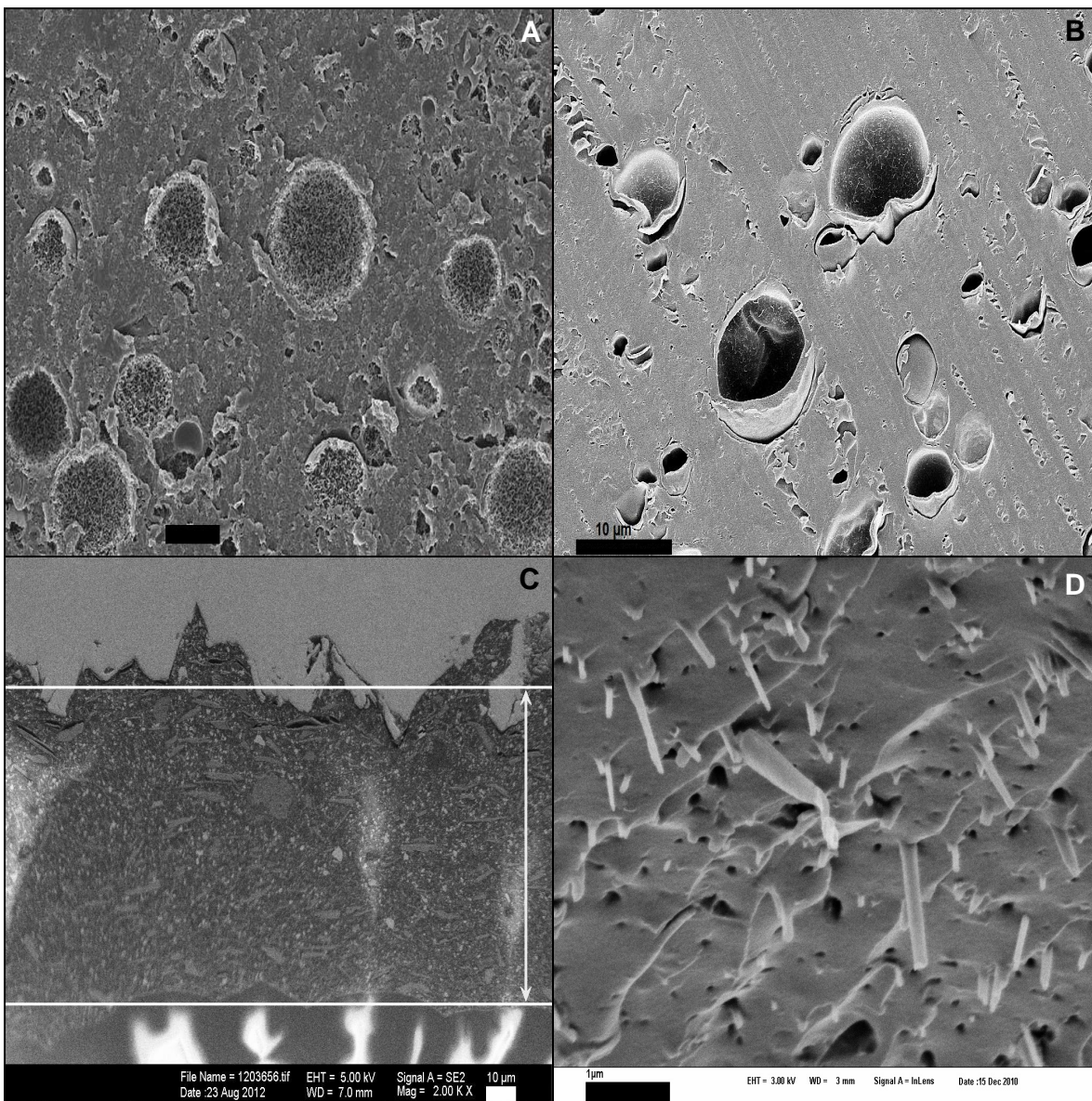
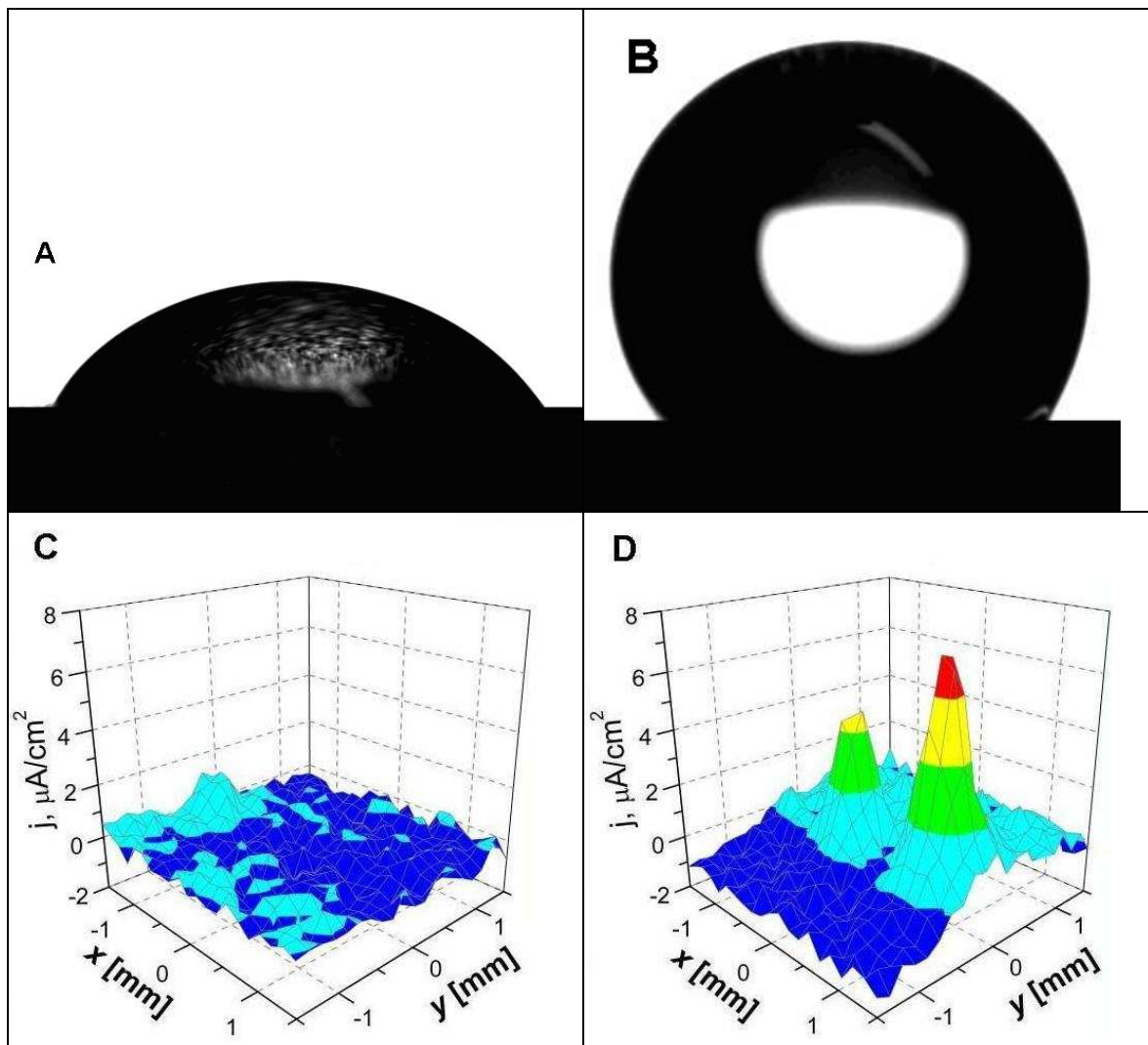


Figure 7. Distribution of nano- and microcontainers in the coating matrix: A – PU microcontainers loaded with the siloxanes mixture in a model epoxy coating [39], scale bar denotes 3 μm; B – PU microcontainers loaded with the

biocide DCOIT in a model epoxy coating, scale bar denotes 10  $\mu\text{m}$ ; C – Halloysite based nanocontainers with PE shells loaded with corrosion inhibitor 8HQ in a model epoxy coating on the steel substrate, scale bar denotes 10  $\mu\text{m}$ , arrow shows the coating thickness; D – Halloysite based nanocontainers with PE shells loaded with corrosion inhibitor benzotriazole (BTA) in an polyester powder coating, scale bar denotes 1  $\mu\text{m}$ .

Containers with polymeric shells of significant polarity such as PU, polyurea (PUa), polyamides etc. are well-dispersible in media with high to moderate polarity because of their essential surface charge stabilizing containers from coagulation. These containers can be successfully introduced into water based coating formulations as for instance shown in Figures 7A and 7B. Core/shell containers with the PU-shells and biocide filling for the self protecting coatings against biofouling are presented in the Figure 7B as already embedded into the polyepoxy coating matrix. These containers were prepared similarly to the pathway described above for the alkoxysilanes filled PU containers. Only the difference was that instead of alkoxysilanes mixture, the dispersed phase of the initial O/W emulsion contained about 55 v/v% of 10 wt% solution of biocide DCOIT in the mixture of octyl- and nonylbenzene. At the same time, polar nature of solvent free powder coatings (polyester and polyepoxy) allowed the homogeneous distribution not only containers with PUa shells but also much more polar halloysites based inorganic containers (Figures 7C, and 7D, respectively).





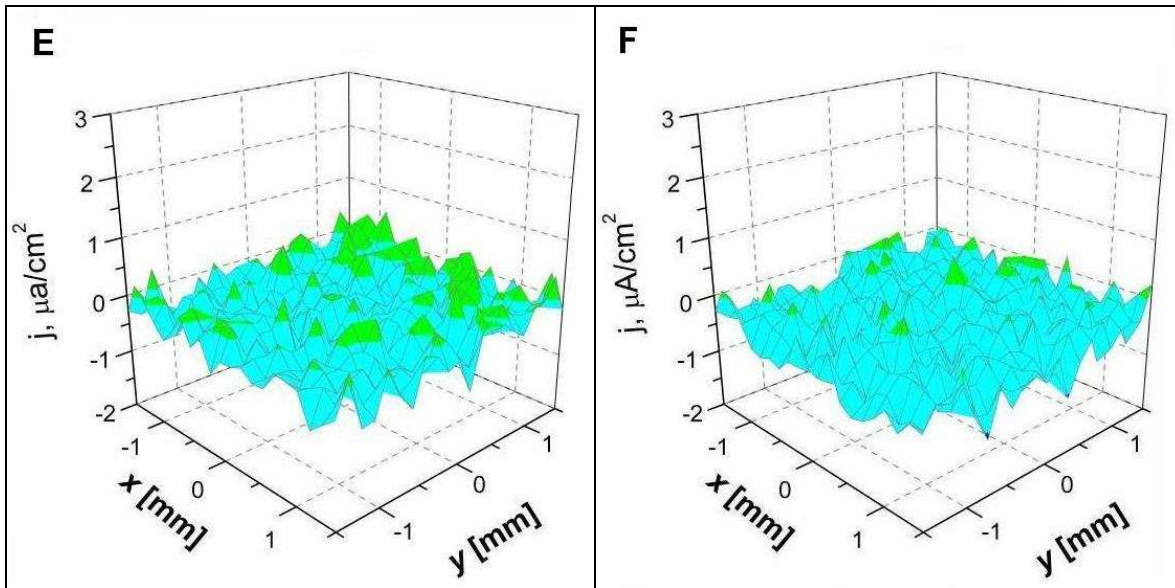


Figure 8. Feedback active functionalities of novel containers based protective coatings [39]. Water repelling: A – contact angle on the pristine aluminum (Al) specimen; B – contact angle on the siloxane treated Al specimen. Anticorrosion performance (corrosion development within 12 h in 0.1 M NaCl): C, D – Al specimen coated with a standard epoxy coating vs. E, F – Al specimen with the same coating doped with 6 wt% of inhibitor loaded microcontainers.

### Protective performance of feedback active container based functional coatings

Self-protecting functionality of novel coatings is determined by the type(s) of active agent(s) loaded in the containers which are incorporated in the coating matrix. Thus anticorrosive, antibacterial, antifouling, dewetting and even various bi- and multifunctional coatings are realizable. Because of the special construction of containers shells their opening is triggered by the factors accompanying the onset or development of destructive event like corrosion, biofouling etc. When the coating is damaged as a result of destructive attack, nearby containers also become mechanically and/or chemically affected. Therefore, the release of the protective agent happens exactly on the damaged or affected site, only on demand, and just in the quantity not exceeding the amount really necessary for the termination of destructive process. This „smart” behaviour of new active coatings leads to very slow depletion of the active agent and very sustained protective performance is achieved comparing with conventional coatings. Moreover, through the fact that some consequences of a certain deterioration process can act as triggers for the release of active agents and finally for the return of the coating to the almost initial non-injured state, the self-recovering of the main protective function of the coating is attained.

Incorporation of PU containers with siloxanes loading (Fig. 5C) into polyepoxy coating (approx. 6 wt% microcontainers in relation to the total mass of the dry coating) led not only to the water-repelling functionality of this coating on the surface of scratches (Figures 8A and 8B), but also to the recovering of its anticorrosion performance. Results obtained by scanning vibrating electrode technique (SVET) showed that in contrast to the conventional polyepoxy coating which after damage could no longer resist the development of corrosion (Figures 8C and 8D), the novel containers based coating demonstrated the gradual weakening of “symptoms” of corrosive process and finally its complete elimination (Figures 8E and 8F).

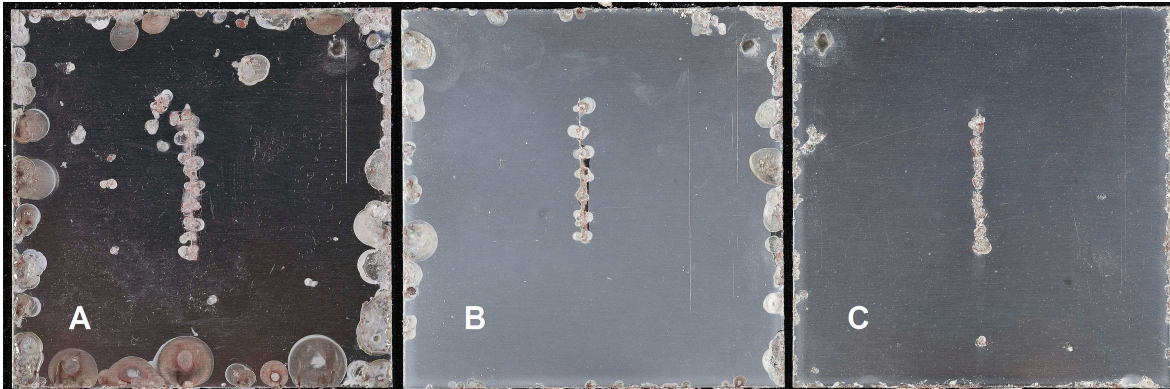


Figure 9. Feedback active functionalities of novel containers based protective coatings. Anticorrosion performance: A – aluminum specimen coated with a standard acrylic coating vs. B – aluminum specimen with the same coating doped with 5 wt% of empty halloysites based nanocontainers and C – aluminum specimen with the same coating doped with 5 wt% of halloysites based nanocontainers possessing PE shells and loaded with corrosion inhibitor mercaptobenzothiazole. CASS test duration – 240 hours.

The halloysite based nanocontainers embedded in an acrylic coating improved its corrosion protection performance significantly compared with standard coatings used previously for the same purpose. The results of Copper Accelerated Acetic Acid Salt Spray Test (CASS-Test) performed in accordance with the specifications of ASTM B368 showed essentially longer maintenance of coating integrity in the area around the artificial scratch and at the cut edges as well as much lower delamination for the coating containing inhibitor loaded halloysites (Figure 9). This enhanced anticorrosion efficiency of novel coating was achieved due to lower depletion of inhibitor from tubuli-shaped containers possessing PE shells making the inhibitor release much more sustained.



Figure 10 shows two another successful applications of inhibitor loaded halloysite based nanocontainers. Powder coated steel specimens were subjected to a neutral salt spray test (NSS-Test) according to ASTM B117 for 500 hours. As one can see, independently from the chemical composition of the coating matrix, introduction of inhibitor loaded nanocontainers led to significant improvement of anticorrosion performance of the coating both for corrosion development on the scratched site as well as for the extend of delamination around the scratch.

## CONCLUSIONS

Novel approach based on the incorporation of active agent filled nano- or microcontainers in the matrix of protective coatings leads to the essential improvement of their resistance to various environmental attacks and to more sustained anticorrosion performance.

Key element of the new type of protective coatings is nano- or microcontainers whose characteristics such as composition, morphology, size etc. determine essentially the protective efficiency of the coating.

Efficient and robust nanocontainers can be prepared on the basis of naturally occurring or pre-formed hollow or mesoporous nanoparticles with subsequent L-b-L polyelectrolyte shell formation.

Fabrication of polymeric & composite nano- or microcontainers via emulsion route is other versatile approach allowing preparation of containers with solid bulk, core/shell or multicompartments (on demand) morphology and size in the range from some  $\mu\text{m}$  to some nm, wide variety of loaded corrosion inhibitors both in solid and liquid state as well as shell components for optimal incorporation in different coatings.

Embedding of containers with different active agents (biocides, sealants etc.) can provide not only the active coatings with specific feedback active functionalities but also multifunctional (simultaneous embedding of several containers types) protective coatings.

## ACKNOWLEDGEMENTS

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## REFERENCES

1. C.M. Dry and N.R. Sottos, "Passive Smart Self-Repair in Polymer Matrix Composite Materials", 1993 North American SPIE Conference on Smart Structures and Materials, Bellingham, WA, Proc. SPIE Vol. 1916, p. 438-444.
2. C.M. Dry, "Procedures developed for self-repair of polymeric matrix composite materials", *Comp. Struct.* 35, 3 (1996): p. 263-269.
3. S.R. White, N.R. Sottos, P.H. Geubelle, J.S. Moore, M.R. Kessler, S.R. Sriram, E.N. Brown, and S. Viswanathan, "Autonomic healing of polymer composites", *Nature* 409, (15 February 2001): p. 794-797.
4. D.G. Shchukin, M.L. Zheludkevich, K.A. Yasakau, S.V. Lamaka, M.G.S. Ferreira, H. Möhwald, "Layer-by-layer assembled nanocontainers for self-healing corrosion protection", *Adv. Mater.* 18, 13 (2006): p. 1672-1678.
5. D.G. Shchukin, H. Möhwald, "Nanocontainers for Entrapment of Corrosion Inhibitors", *Adv. Funct. Mater.* 17, 9 (2007): p. 1451-1458.
6. D.G. Shchukin, H. Möhwald, "Self-repairing coatings containing active nanoreservoirs", *Small* 3, 6 (2007): p. 926-943.
7. A.E. Hughes, I.S. Cole, T.H. Muster, R.J. Varley, "Designing green, self-healing coatings for metal protection", *NPG Asia Mater.* 2, 4 (2010): p. 143-151.
8. B.J. Blaiszik, S.L.B. Kramer, S.C. Olugebefola, J.S. Moore, N.R. Sottos, and S.R. White, "Self-Healing Polymers and Composites", *Annu Rev Mater Res* 40, (5 April 2010): p. 179-211.
9. X. Wang, C. Liu, X. Li, F. Li, S. Zhou, "Photodegradation of 2-mercaptobenzothiazole in the  $\gamma\text{-Fe}_2\text{O}_3$ /oxalate suspension under UVA light irradiation", *J. Hazard. Mater.* 153, 1-2 (2008): p. 426 - 433.
10. E. A. Ferreiro, S. G. De Bussetti, and A. K. Helmy, "Sorption of 8-Hydroxyquinoline by some clays and oxides", *Clays Clay Miner.* 36, 1 (1988): p. 61 - 67.
11. S.K. Ghosh, *Self-healing Materials: Fundamentals, Design Strategies, and Applications* (Weinheim, WILEY, 2009), p. 102.
12. E.W. Brooman, "Modifying organic coatings to provide corrosion resistance Part I: Background and general principles", *Met. Finish.* 100, (January 2002): p. 48-53.
13. E.W. Brooman, "Modifying organic coatings to provide corrosion resistance: Part II - inorganic additives and inhibitors", *Met. Finish.* 100, (May 2002): p. 42-53.
14. E.W. Brooman, "Modifying organic coatings to provide corrosion resistance Part III: organic additives and conducting polymers", *Met. Finish.* 100, (June 2002): p. 104-110.
15. A.J. Vreugdenhil and M.E. Woods, "Triggered Release of Molecular Additives from Epoxy-Amine Sol gel Coatings", *Prog. Org. Coatings* 53, 2 (2005): p. 119-125.

16. D. Raps, T. Hack, J. Wehr, M.L. Zheludkevich, A.C. Bastos, M.G.S. Ferreira, O. Nuyken, "Electrochemical study of inhibitor-containing organic-inorganic hybrid coatings on AA2024", *Corros. Sci.* 51, 5 (2009): p. 1012–1021.
17. Y. Lvov, R. Price, *Bio-Inorganic Hybrid Nanomaterials*, Eds.: E. Ruiz-Hitzky, K. Ariga, Y. Lvov, (London, Berlin, Wiley, 2008), p. 454–480.
18. E. Joussein, S. Petit, J. Churchman, B. Theng, D. Righi, and B. Delvaux, "Halloysite clay minerals – a review", *Clay Minerals* 40, 4 (2005): p. 383-426.
19. S. K. Poznyak, J. Tedim, L. M. Rodrigues, A. N. Salak, M. L. Zheludkevich, L. F. P. Dick, and M. G. S. Ferreira, "Novel Inorganic Host Layered Double Hydroxides Intercalated with Guest Organic Inhibitors for Anticorrosion Applications", *ACS Appl. Mater. Interfaces* 1, 10 (2009): p.2353 – 2362.
20. G. Williams and H. N. McMurray, "Anion-Exchange Inhibition of Filiform Corrosion on Organic Coated AA2024-T3 Aluminum Alloy by Hydrotalcite-Like Pigments", *Electrochem. Solid-State Lett.* 6, 3 (2003): p. B9 – B11.
21. G. Williams and H. N. McMurray, "Inhibition of Filiform Corrosion on Polymer Coated AA2024-T3 by Hydrotalcite-Like Pigments Incorporating Organic Anions", *Electrochem. Solid-State Lett.* 7, 5 (2004): p. B13 – B15.
22. J. Tedim, M. L. Zheludkevich, A. N. Salak, A. Lisenkov and M. G. S. Ferreira, "Nanostructured LDH-container layer with active protection functionality", *J. Mater. Chem.* 21, 39 (2011): p. 15464 – 15470.
23. D.O. Grigoriev, M.F. Haase, N. Fandrich, A. Latnikova, D.G. Shchukin, "Emulsion route in fabrication of micro and nanocontainers for biomimetic self-healing and self-protecting functional coatings", *Bioinspired, Biomimetic and Nanobiomaterials (BBN)* 1, 2 (2012): 101-116.
24. D.O. Grigoriev, T. Bukreeva, H. Möhwald and D.G. Shchukin, "New Method for Fabrication of Loaded Micro- and Nanocontainers: Emulsion Encapsulation by Polyelectrolyte Layer-by-Layer Deposition on the Liquid Core", *Langmuir* 24, 3 (2008): p. 999–1004.
25. H. Wackerbarth, P. Schön, and U. Bindrich "Preparation and Characterization of Multilayer Coated Microdroplets: Droplet Deformation Simultaneously Probed by Atomic Force Spectroscopy and Optical Detection", *Langmuir* 25, 5 (2009): p. 2636–2640.
26. M.V. Lomova, G.B. Sukhorukov, and M.N. Antipina, "Antioxidant Coating of Micronsize Droplets for Prevention of Lipid Peroxidation in Oil-in-Water Emulsion", *ACS Nano* 2, 12 (2010): p. 3669–3676.
27. K. Köhler, G.G. Shchukin, G.B. Sukhorukov, and H. Möhwald, "Drastic Morphological Modification of Polyelectrolyte Microcapsules Induced by High Temperature", *Macromolecules* 37, 25 (2004): p. 9546–9550.
28. D.G. Shchukin, D.A. Gorin, H. Möhwald, "Ultrasonically induced opening of polyelectrolyte microcontainers", *Langmuir* 22, 17 (2006): p. 7400–7404.
29. T. Mauser, C. Déjugnat, H. Möhwald, and G.B. Sukhorukov, "Microcapsules Made of Weak Polyelectrolytes: Templating and Stimuli-Responsive Properties", *Langmuir* 22, 13 (2006): p. 5888–5893.
30. B.P. Binks, "Particles as surfactants – similarities and differences", *Curr Opin Colloid Interface Sci.* 7, 1-2 (2002): p. 21–41.
31. J. Frelichowska, M.-A. Bolzinger, Y. Chevalier, "Pickering emulsions with bare silica", *Colloids Surf A* 343, 1-3 (2009): p. 70–74.
32. U.T. Gonzenbach, A.R. Studart, E. Tervoort, and L.J. Gauckler, "Ultrastable Particle-Stabilized Foams", *Angew Chem Int Ed* 45, 21 (2006): p. 3526–3530.
33. M. Schmitt-Rozières, J. Krägel, D.O. Grigoriev, L. Liggieri, R. Miller, S. Vincent-Bonnieu, and M. Antoni, "From Spherical to Polymorphous Dispersed Phase Transition in Water/Oil Emulsions", *Langmuir* 25, 8 (2009): p. 4266–4270.
34. B.P. Binks and S.O. Lumsdon, "Influence of Particle Wettability on the Type and Stability of Surfactant-Free Emulsions", *Langmuir* 16, 23 (2000): p. 8622–8631.
35. M.F. Haase, D. Grigoriev, H. Moehwald, B. Tiersch, and D.G. Shchukin, "Encapsulation of Amphoteric Substances in a pH-Sensitive Pickering Emulsion", *J Phys Chem C* 114, 41 (2010): p. 17304–17310.

36. J.K. Ferri, C. Philippe, N. Gorevski, T.P. Russell, Q. Wang, A. Böker and A. Fery, "Separating membrane and surface tension contributions in Pickering droplet deformation", *Soft Matter* 4, 11 (2008): p. 2259–2266.
37. D. Grigoriev, R. Miller, D. Shchukin, and H. Möhwald, "Interfacial Assembly of Partially Hydrophobic Silica Nanoparticles Induced by Ultrasonic Treatment", *Small* 3, 4 (2007): p. 665–671.
38. A. Latnikova, D.O. Grigoriev, H. Möhwald and D.G. Shchukin, "Capsules Made of Cross-Linked Polymers and Liquid Core: Possible Morphologies and Their Estimation on the Basis of Hansen Solubility Parameters", *J. Phys. Chem. C* 116, 14 (2012): p. 8181–8187.
39. A. Latnikova, D.O. Grigoriev, J. Hartmann, H. Möhwald, and D.G. Shchukin, "Polyfunctional active coatings with damage-triggered water-repelling effect", *Soft Matter* 7, 2 (2011): p. 369–372.
40. M. Barrère and K. Landfester, "High Molecular Weight Polyurethane and Polymer Hybrid Particles in Aqueous Miniemulsion", *Macromolecules* 36, 14 (2003): p. 5119–5125.
41. B. Abismaïl, J.P. Canselier, A.M. Wilhelm, H. Delmas, C. Gourdon, "Emulsification by ultrasound: drop size distribution and stability", *Ultrason Sonochem* 6, 1-2 (1999): p. 175–183.
42. D. Borisova, H. Möhwald and D.G. Shchukin, "Influence of Embedded Nanocontainers on the Efficiency of Active Anticorrosive Coatings for Aluminum Alloys Part I: Influence of Nanocontainer Concentration", *ACS Appl. Mater. Interfaces* 4, 6 (2012): p. 2931–2939.
43. D. Borisova, H. Möhwald and D.G. Shchukin, "Influence of Embedded Nanocontainers on the Efficiency of Active Anticorrosive Coatings for Aluminum Alloys Part II: Influence of Nanocontainer Position", *ACS Appl. Mater. Interfaces* 5, 1 (2013): p. 80–87.
44. M. J. Hollamby, D. Fix, I. Dönch, D. Borisova, H. Möhwald, and D. Shchukin, "Hybrid Polyester Coating Incorporating Functionalized Mesoporous Carriers for the Holistic Protection of Steel Surfaces", *Adv. Mater.* 23, 11 (2011): p. 1361–1365.

## FIGURE CAPTIONS

Figure 1. Illustration of the scratch propagation along the protective container based coating on the metal substrate affecting the embedded containers.

Figure 2. Mesoporous or hollow micro- and nanoparticles used for the preparation of containers ceramic core: A – halloysite nanotubes, scale bar below denotes 200 nm; B - spherical mesoporous silica (SMS) nanoparticles, scale bar denotes 100 nm; C - spherical hollow silica (SHS) nanoparticles, scale bar denotes 200 nm; D – mesoporous TiO<sub>2</sub> nanoparticles, scale bar below denotes 200 nm; E – commercially available silica microparticles, scale bar denotes 1 μm; F – commercially available aluminium modified silica submicroparticles, scale bar denotes 200 nm. For more details see text.

Figure 3. Ceramic container cores filled with inhibitors: A, B – empty halloysites and halloysites filled with ammonium molybdate, respectively; C – SHS silica particles filled with mercaptobenzothiazole (MBT); D – commercially available silica microparticles filled with cerium nitrate; E – commercially available aluminium modified silica microparticles filled with sodium hexafluorotitanate. For more details see text.

Figure 4. Schema of assembly steps at the preparation of ceramic particle based nano- or microcontainers. The second step on the left top and bottom pictures represents the L-b-L alternate PE adsorption halloysite nanotubes and mesoporous ceramic particles, respectively. Microphotographs on the right show the surface of mesoporous ceramic particle before (top) and after (bottom) deposition of PE multilayer, scale bars denote in both cases 200 nm.

Figure 5. Micro- and nanocontainers obtained by use of different chemical and physical interfacial phenomena: A – containers from droplets of O/W emulsion prepared by PE L-b-L interfacial adsorption technique [24], scale bar below denotes 3 μm; B – containers on the basis of Pickering emulsion with subsequent particles locking by PE L-b-L interfacial deposition [23], scale bar denotes 2 μm; C – Microcontainers with Polyurethane (PU) shells loaded with the siloxanes mixture prepared by interfacial polyaddition reaction [39], scale bar denotes 2 μm; D & E – Nanocontainers with silica shell loaded with corrosion inhibitor mercaptobenzothiazole, TEM and EDX pictures, scale bar denotes 1 μm; F – Polyepoxy micro- and nanocontainers filled with the corrosion inhibitor methylbenzothiazole (MeBT) obtained by *in-situ* polymerization of O/W emulsion [23], scale bar denotes 2 μm.

Figure 6. Release kinetics from containers freely distributed in media: A – Halloysite based containers enveloped in PE shell loaded with benzotriazole at different pH in the aqueous medium; B – containers with polyurethane shells loaded with biocide 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT) in ethanol medium; C – SHS silica containers loaded with inhibitor 8-Hydroxyquinoline (8-HQ) at different pH in the aqueous medium.

Figure 7. Distribution of nano- and microcontainers in the coating matrix: A – PU microcontainers loaded with the siloxanes mixture in a model epoxy coating [39], scale bar denotes 3 μm; B – PU microcontainers loaded with the biocide DCOIT in a model epoxy coating, scale bar denotes 10 μm; C – Halloysite based nanocontainers with PE shells loaded with corrosion inhibitor 8HQ in a model epoxy coating on the steel substrate, scale bar denotes 10 μm, arrow shows the coating thickness; D – Halloysite based nanocontainers with PE shells loaded with corrosion inhibitor benzotriazole (BTA) in a polyester powder coating, scale bar denotes 1 μm.

Figure 8. Feedback active functionalities of novel containers based protective coatings [39]. Water repelling: A – contact angle on the pristine aluminum (Al) specimen; B – contact angle on the siloxane treated Al specimen. Anticorrosion performance (corrosion development within 12 h in 0.1 M NaCl): C,



D – Al specimen coated with a standard epoxy coating vs. E, F – Al specimen with the same coating doped with 6 wt% of inhibitor loaded microcontainers.

Figure 9. Feedback active functionalities of novel containers based protective coatings. Anticorrosion performance: A – aluminum specimen coated with a standard acrylic coating vs. B – aluminum specimen with the same coating doped with 5 wt% of empty halloysites based nanocontainers and C – aluminum specimen with the same coating doped with 5 wt% of halloysites based nanocontainers possessing PE shells and loaded with corrosion inhibitor mercaptobenzothiazole. CASS test duration – 240 hours.

Figure 10. Feedback active functionalities of novel containers based protective coatings. Anticorrosion performance I: A – steel specimen coated with a standard polyepoxy powder coating vs. B – steel specimen coated with the same coating doped with 5 wt% of halloysites based nanocontainers possessing PE shells and loaded with corrosion inhibitor 8-HQ and C – steel specimen coated with the same coating doped with 5 wt% of halloysites based nanocontainers possessing PE shells and loaded with corrosion inhibitor 1H-benzotriazole;

Anticorrosion performance II: D – steel specimen coated with a standard polyester powder coating vs. E – steel specimen coated with the same coating doped with 5 wt% of microcontainers possessing polyepoxy shells and loaded with corrosion inhibitor methylbenzothiazole and F – steel specimen coated with the same coating doped with 5 wt% of microcontainers possessing polyepoxy shells and loaded with corrosion inhibitor 8-HQ; For more details see text.