MUST – Final Publishable Report

Overall summary

The advanced coatings and adhesives based on innovative combinations of nanotechnologies for improved safety, extended service life and aesthetic value, are today a worldwide topmost research area with an outstanding technical and industrial impact. The main objective of MUST project was the development of effective environmentally-friendly multi-level active protection systems for structural metallic materials used in future vehicles. The approach of MUST is based on a combination of advanced polymeric matrixes and active nanocontainers providing healing effects. A significant improvement of the durability and performance of a protective coating becomes evident if early stage degradation phenomena are recovered and the barrier properties of the coating are kept for a longer time.

Novel functional nanocontainers capable of storage of active agents and their controllable release triggered by specific conditions such as pH, temperature, mechanical impact, water and chlorides were developed in the project. These agents have healing properties and can therefore repair damages in coatings and protect underlying metallic substrate. The top facilities for nanocontainers fabrication and encapsulation of active species and the most modern characterization techniques were synergistically combined within MUST for achieving these edge research goals. The production technology of the most successful nanocontainers was scaled up during the project from gram-scale in the lab to several hundred liters batches in the pilot scale.

New experimental techniques and analytical methodologies have been specifically developed to fulfill the needs of the project since the topic of self-healing coatings is relatively new and the existing experimental protocols for investigation of the self-healing effects are very limited. In addition, an algorithm and computational code for the multilevel protection is developed for systems consisting of multilayer coatings with water traps and containers with corrosion inhibitor that can be released upon internal trigger (salt concentration, pH), providing control on water and corrosive ions transport throughout the coating.

Novel technologies for active corrosion protection of cars and aircrafts were developed in MUST. Specifically, the addition of functional nanocontainers and nanotraps to automotive pre-treatments and primers led to significant improvement of the performance in terms of long-term corrosion protection and coating adhesion properties. The corresponding technologies are patented and are on the way to commercialization in the form of new products within the next few years.
The most successful products originated from MUST are:

- automotive self-healing pre-treatments with nanocontainers of corrosion inhibitors;
- active anti-corrosion primer with nanotraps for automotive applications;
- multi-functional aeronautical primer with nanocontainers;
- structural adhesives with inhibiting nanocontainers for cars.

The protective solutions developed in MUST provide sustainable components and offer the chance for decreasing cost by reducing process steps during pre-treatment and in paint shop, regardless of the specific type of transport industry. The performance in terms of corrosion protection still has to be optimized on the upscaled industrial level during the post-project phase in order to meet the good coupon level properties. An important effect on competitiveness is obtained not only by meeting but even surpassing the current environmental regulations.

MUST has produced some of the latest advances in the topic and has become worldwide recognized. Above 50 scientific publications in international journals of high impact, dissemination activities within the general public (including 1 Website, 4 public workshops, videos and news) and transfer of technology via filing of 3 patents and the creation of 1 spin-off company are among the major impacts of MUST.

This has brought MUST to one of the most successful projects funded by the EU Commission, producing tangible objectives, paving the way for more competitive markets and technologies and strengthening the EU competitiveness.

Summary description of project context and objectives

The destructive effect of environment and the corrosion induced degradation are the important factors which determine the economical service life of a vehicle or its components. The application of organic coatings is the most common and cost effective method of improving protection and durability of metallic structures.

The long term performance of organic coatings is by nature subject to chemical and physical aging processes. One strategy to improve the in-service life of protective coatings is to respond to these conditions with healing reactions. This ability is expected to be most effective if it is reacting at certain stages of degradation with different healing processes. A significant improvement of the durability of protective coating is evident if early stage degradation phenomena are recovered and e.g. the decrease of the barrier properties of the coating is postponed to longer exposure times.

The ***main vision*** of the project MUST is to develop new active multi-level protective self-healing coatings and adhesives for future vehicle materials. These materials will be based on "smart" release nanocontainers incorporated into the polymer matrix of current commercial products. A nanocontainer (or nanoreservoir) is a nanosized volume filled with an active substance confined in a porous core and/or a shell which prevents direct contact of the active agent with the adjacent environment.

The ***main objective*** of the MUST project is the design, development, upscaling and application of novel multi-level protection systems like coatings and adhesives for future vehicles and their components to improve radically the long-term performance of metallic substrates and structures. A **multi-level self-healing approach** will combine - within one system - several damage prevention and reparation mechanisms, which will be activated depending on type and intensity of the environmental impact.

The ***main novel idea*** suggested in MUST is the multi-level protection approach based on functional nanocontainers. Several self-healing protection mechanisms were suggested before but were never combined together in the same polymer system. The innovative idea of this project is a gradually active protection response of the coating depending on the nature and the degree of impacts from external environment.

The multi-level self-healing concept is based on gradual active feed-back of the protective systems to the environmental conditions as illustrated in Figure 1. Different active components in the protective system will be able to respond to four different types and levels of impacts imposed to the coating:

- The first level of protection will be provided by the incorporation of nanotraps (nanoparticles able to absorb aggressive/corrosive species if their level in the coating or adhesive exceeds a critical value).

- The <u>second level</u> is based on the use of water displacing compounds, which are released from nanocontainers as soon as the first microdefects appear in the polymer matrix.
- Further growth of the defects will trigger the release of polymerizable precursors entrapped in other nanocapsules <u>(third level of protection</u>, see Figure 1). Then a new thin polymer film will be formed, cover the damaged area and repair the layer, preventing crack propagation.
- The <u>highest level of protection</u> will be based on encapsulation of organic and inorganic corrosion inhibitors in different types of nanocontainers (10 – 100 nm in size) acting on demand and suppressing corrosion and delamination processes occurring in open defects or at cut edges.

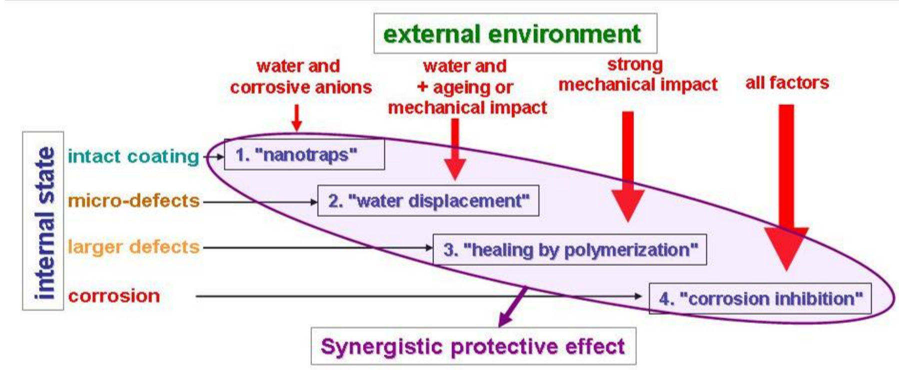

Figure 1 - Illustration of the multi-level protection approach proposed in MUST.

The **MUST consortium** is created using an objective driven approach as a driving force. The industries directly involved in the production chain of materials for different transport industries are represented in the project. The project is organized in three main branches starting from academic and research institutions continuing through pigment and pre-treatment/paint/adhesive producers toward to transportation industry end users. The pre-treatment, paint and adhesive producers will play one of the key roles in the project since they will directly benefit from the obtained results. The remaining industrial participants, especially end-users, will also be strongly involved into the coordination and the decision making process. The academic and research centres are selected for the project on the basis of excellence in particular area providing complementarities of expertise and skills needed for a successful project realization. There is a balanced structure of the consortium with partners from academic and research centres and partners from industry (automotive, aerospace and maritime), SMEs and pre-treatment/paint/adhesive suppliers from different European countries.

Main S&T results/foregrounds

WP2-SP1

The main target of SP1 - Development of nanocontainers involves design, development and testing of the nanocontainers, following both the multi-level active protection and the self-healing ability of the containers. To improve protection and functional (response) characteristics of nanocontainers, their shell can be functionalized using active compounds (e.g., metal and magnetic nanoparticles, polyelectrolytes) by either chemical binding or LbL electrostatic adsorption. The nanocontainers encapsulating various active agents are embedded as additives in model coating systems for further investigations on the different levels of corrosion protection in sub-project 2.

The following procedures were evaluated to get maximal encapsulation yield:

1. Capturing by reversible opening the pores of the container shell by different external factors (e.g., pH, solvent variation).
2. Precipitation followed by shell formation and modification.
3. Embedding (adsorbing) in a porous (empty) host also followed by shell assembly.
4. Impregnation from inhibitor-containing solution under vacuum pumping.
5. Ultrasonic or mechanic formation of oil-in-water emulsions accompanied by shell assembly with the active agent dissolved in the oil phase
6. Immobilization of inhibiting ions in ion-exchange pigments

The mechanism for the controlled release of active materials depends on the kind of nano container. Depending on the type of the nanocontainers, we envisaged 3 triggering mechanisms for the release of active materials:
- pH-triggering for containers with polyelectrolyte shell, shell containing weak polyacids/polybases, shell assembled by H-bonding;
- triggering by electromagnetic irradiation: for containers with the shell loaded with light-sensitive metal nanoparticles (Ag, Au) and azo-polymers;
- triggering by mechanic damage (opening) of the containers.

The main achievements according to the SP1 tasks are as following.

1st level of protection – nanotraps for water molecules and corrosion ions

Layered double hydroxides (LDHs) were taken as main material for this protection level. During the project execution, structural and morphological characterization and corrosion performance with anionic inhibitors has been discussed in detail. The structure of LDHs can be considered as versatile from the corrosion standpoint: being anion-exchangers, the LDHs can release the intercalated active material by exchange with aggressive ions from the surroundings (including chlorides, sulphates and carbonates). On the other hand, these structures may respond indirectly to pH: in high pH conditions the inhibitor can be exchanged with hydroxyl anions whereas in low pH conditions the LDHs start to dissolve and the inhibiting anions are released in the solution. In the release studies, two different types of LDHs were studied: Zn(2)-Al-MBT LDHs prepared by ion-exchange and Mg(3)-Al-MBT prepared by calcination-rehydration method.

On the next stage, the grafting of the clay nanotraps was performed in order to improve their dispersion in the coating matrix. The aim was to attach initiating groups for polymerization directly to the surface of the clay, taking advantage of the hydroxyl groups present. The initiator could be attached to the hydroxyl groups either by esterification or silylation. The polymerization method used in the modification was ATRP and as an initiator 2-bromo isobutyrylbromide was used. Three different clays (montmorillonite ($(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2$), sepiolite ($Mg_4Si_6O_{15}(OH)_2$) and halloysite ($Al_2Si_2O_5(OH)_4$)) have been modified with polymers. To make the clay composites

compatible with water based primers the modification of clay was done with water soluble polymers. For this PNIPAM and later PDMAEMA were chosen and the polymerizations were conducted with according monomers.
Another type of nanotraps, chloride nanotraps, was synthesized by modification of silicon dioxide templates. In order the nanospheres to be modified, GPTMS was added and the reactant mixture is left under stirring for 10 hours. The size of the resulting nanotraps is 125 ± 20 nm. Their ability to trap chloride anions was testing with solutions of 0.5 M NaCl and 4.33 M HCl. It was found that after the exposure of the nanotraps into the above solutions, they consist of 2.5 % w/w Cl^-.

2nd level of protection – micro-/nanocontainers with water displacing/repelling agents

The best examples of the nanocontainers with water displacing/repelling activity developed in MUST project are water nanotraps and polyurethane capsules with water-repelling agent.
Polymetacrylic water nanotraps were prepared by distillation precipitation polymerization. The ability of PMAA nano-microspheres to absorb water was succeeded by conversion of carboxylic groups to the corresponding sodium salts adding sodium hydroxide solution. The water nanotraps could be regenerated from the hydrogel by washing with an organic solvent, such as ethanol.
Polyurethane capsules with water-repelling agent were synthesized via interfacial polymerization. Resulting containers loaded with a mixture of alkoxysilanes were introduced into a conventional epoxy-coating. When the integrity of the coating is damaged, containers open and their content flows into the crack and spreads on the substrate surface. Exposure to the aggressive ambient medium with high humidity initiates the reaction of the alkoxysilanes with hydroxyl groups on the substrate surface producing highly hydrophobic film thus passivating the substrate surface.

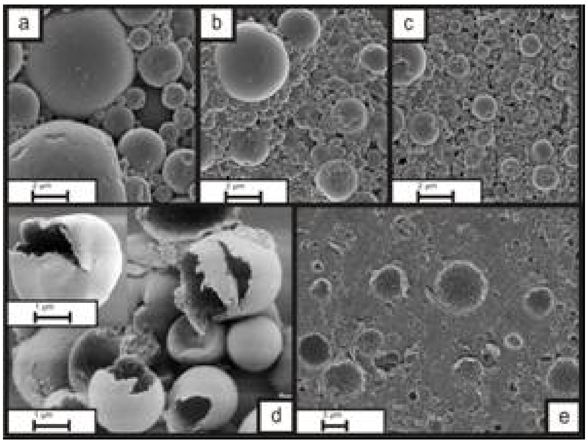

Figure 1. SEM image of microcontainers synthesized at different speed of the stirrer: a) 11000 min^{-1} b) 16000 min^{-1} and c) 22000min^{-1}. d) SEM image of crushed microcapsules. e) SEM image of the cut of the coating with high content of microcontainers incorporated.

The mean size of the resulting micro- and nanocontainers can be varied simply by changing the speed of the stirring on the emulsification step without noticeable influence on their morphology. SEM images of "crushed" containers clearly show their core-shell structure. EDX measurements show that the content of encapsulated alkoxysilanes was about 30% wt., which is in well agreement with the theoretical value.
SVET and visual corrosion test clearly confirm the effectiveness of the proposed self-healing water-repelling system. All control samples showed the corrosion onset already 6 hours after immersion in 0.1 M NaCl solution (the process starts with the blackening of the defect surface followed by appearance of white fluffy precipitate within the groove of the scratched regions). In contrast, the samples show after the release of the water-repelling agent no visual evidence of corrosion even 3 days after exposure (the surface of the scratch remains shiny).

3rd level of protection – microcontainers with healing agents and catalyst

The preparation of PU containers with healing agents followed the procedure of membrane polymerization, at which MTEOS was mixed with monomer DVL in toluene. Membrane with pore size of 200nm was used. TOPCOAT films containing 10 wt % of capsules in benzyl alcohol were prepared on both Mylar and metallic substrates. Containers showed a wide range of particle size distribution. Two different washing processes were used to wash the PU capsules containing prepolymer; (1) filtration; (2) centrifuge (2000 rpm/10min). The samples seemed to be completely collapse after centrifugation while filtration seems to impose less damage to the capsules.

In order to demonstrate the self-repairing properties of hybrid PU-prepolymer microcontainers, PU films containing 3, 9 and 22 wt% microcontainers have been prepared. Such prepared samples were scratched with a scalpel ca. 10 µm wide and observed by optical microscope. Optimal curing conditions of prepolymer are known to be ca. 8 hours in 80% humidity. Comparing to reference film without PU microcontainers, after scratching PU film with 3 wt% of capsules, a white colour appeared immediately after the scratch was formed; still, the gap was not completely filled with a liquid. The curing effect was more distinct for the film containing 9 wt% of PU capsules. A complete curing of the gap was observed for a film with the highest amount of PU microcontainers (22 wt %). As a result of test, release of prepolymer and healing effect was demonstrated.

4th level of protection – nanocontainers with corrosion inhibitor

The optimization of method for encapsulation of the corrosion inhibitor, methylbenzothiazole (MBT), by layer-by-layer adsorption of polyelectrolytes was demonstrated. The oil phase for capsules' liquid cores was prepared by dissolution of AOT in 10ml of chloroform solution containing corrosion inhibitor. Final concentration of MBT in oil phase was 6%. Emulsion droplets were formed by addition of AOT/chloroform to polycation (PDADMAC) solution during mixing with a magnetic stirrer. After adsorption of the first layer of PDADMAC and formation of suspension of liquid cores stabilized by AOT/PDADMAC interfacial complexes, the consecutive layers of polyelectrolytes were formed by layer-by-layer technique using the saturation method. Therefore, the multilayer shells (PDADMAC/PSS/PDADMAC) were constructed.

A microemulsion of DMSO (DMSO+MBT) in water is then chosen to prepare the nanocontainers. AOT and 1-butanol were used as surfactant and cosurfactant to prepare DMSO (DMSO with MBT) emulsion. The droplets were further stabilized by forming an organosilica-based shell with addition of octyltriethylsilane (OCTEO) and aminopropyltrimethoxy silane (APS). Further on another surfactant, Triton was chosen instead of AOT in order to improve the encapsulation of MBT inside the nanocontainer.

Monodisperse, mesoporous silica nanoparticles and their application as nanocontainers loaded with corrosion inhibitor (1H-benzotriazole (1H-BTA)). The developed porous system of mechanically stable silica nanoparticles exhibits high surface area (~ 1000 $m^2 \cdot g$-1), narrow pore size distribution (d ~ 3 nm) and large pore volume (~ 1 mL·g-1). As a result, a sufficiently high uptake and storage of the corrosion inhibitor in the mesoporous nanocontainers was achieved. The successful embedding and homogeneous distribution of the 1H-BTA loaded monodisperse silica nanocontainers improve the corrosion resistance of the steel substrates in 0.1 M sodium chloride solution. The enhanced corrosion protection of this newly developed active system in comparison to the passive coating during the corrosion process was observed by the scanning vibrating electrode technique (SVET).

Copper oxide nanocontainers were synthesized using copper acetate in 2-propanol in a three-necked flask under stirring. Copper oxide nanocontainers were synthesized in a new simple and quick way. Their size was characterized by SEM measurements and was ranged between 150 to 360 nm. Loaded nanocontainers were tested for antifouling properties.

The surface of cerium molybdate and cerium titanium oxide nanocontainers was chemically modified in order the nanocontainers to be well dispersed in MUST partner's solutions. Two

methods were used for the surface modification of nanocontainers. The first method includes the addition of the nanocontainers in water or ethanol solution of aminopropyltriethoxysilane under stirring for 12 hours. The result is activation of the surface with amine groups. The second method includes the insertion of nanocontainers in a water solution of ammonium hydroxide. After 10 hours of stirring, the surface contains amino and hydroxyl groups.
Being LDH-VOx one of the most important systems studied so far in the frame of MUST project, it is necessary to study the release of vanadate anions from LDHs. During the release studies the solution pH was found to be between 7 and 8. The obtained results reveal that the release of vanadate species occurs in a two-stage, for short (during first 5 hours) and long timescales (after 24 hours). These results are in agreement with the results found for LDH-MBT, showing that release of LDHs, as expected, is intrinsic to LDH materials rather than to the intercalated species.
The release of inhibitor 2-mercaptobenzothiazole (2-MB) from 25.36% w/w loaded cerium titanium oxide nanocontainers was studied via Electrochemical Impedance Spectroscopy. In the low frequency region, it can be seen that the total value of impedance is about one order of magnitude higher for the specimens immersed in the 0.05 M NaCl solution containing the nanocontainers loaded with inhibitors. It can be clearly seen that the chemical compound worked as corrosion inhibitors comparing to the solution without loaded nanocontainers.

WP2-SP2

Subproject 2 (SP2) mainly considered fundamental investigations of the dispersion, reactivity and self-healing properties of nanocontainers and their combinations in polymeric and inorganic layers. Functional nanocontainers with various host structures and encapsulated additives as developed in SP 1 were embedded in model coatings and adhesive systems, in order to study the mechanisms and kinetics of nanocontainer based processes on the respective protection levels. The structure and the elemental composition of the nanocontainer-impregnated coatings were investigated by means of microscopic (SEM, TEM, AFM) and spectroscopy techniques (FTIR, Raman, XPS). Detailed electrochemical investigations and evaluation of the corrosion resistance of the modified coatings were achieved by means of conventional (e.g. current-density potential curves, electrochemical impedance spectroscopy (EIS)) and new advanced localized (Scanning Vibrating electrode (SVET), Scanning Ion Electrode Techniques (SIET), Localised Electrochemical Impedance Spectroscopy (LEIS) and the Scanning Kelvin Probe (SKP)) electrochemical techniques. Selected corresponding experimental results were used as input parameters for simulation and modelling in SP3.

The main achievements according to the SP2 tasks are described in the following.

Design and evaluation of model coatings

Suitable matrices compatible with the stimuli responsive nanocontainers as additives were designed and evaluated. Pretreatments, primer systems, polyelectrolytes, epoxy and PU- based coatings are some examples for the used model coatings.

Understanding of the interaction between the nanocontainers and the polymeric matrix

The interaction between the nanocontainers and the polymeric matrix was studied in order to improve the understanding of the compatibility of the nanocontainers and the respective coating matrix as well as to be able to predict the mechanical and barrier properties of the functional composite coating. Laboratory tests on the compatibility of nanocontainers in the paints were done on liquid coating materials as well as on cured coatings by SEM characterizations. Different containers were analysed with regard to the different corrosion protection level. For example, LDH and TiO_2 nanocontainers (loaded with inhibitor), developed for the 4th level of corrosion protection, PU microcontainer (loaded with MTES, prepolymer, MBT) for the 2nd, 3rd and 4th level of corrosion protection.

Preparation of model defects and patterned coating systems

Defined small defects of varying size and geometry were prepared by the Focused Ion Beam Technique (FIB) or stretch forming and were analysed by a combination of integral and localized electrochemical techniques to extract information for a better understanding of the corrosion processes and corresponding repair of active microscopic defects formed on thin coatings containing inhibitor filled containers [1].

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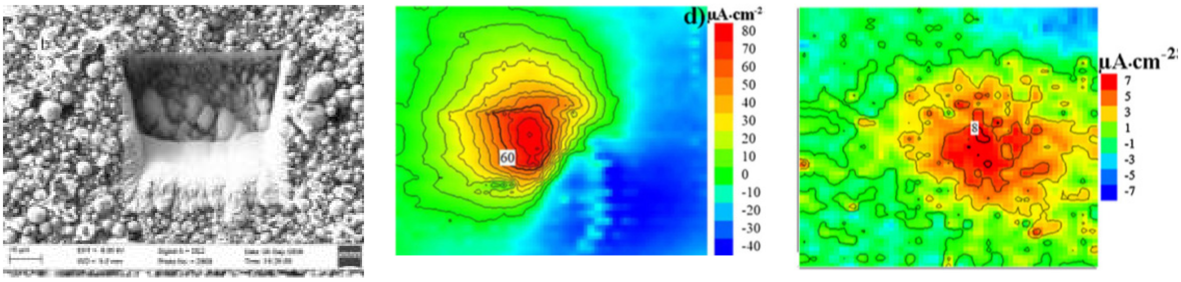

Figure 1. FIB defect formed in a primer coating (a). SVET map of ionic current density of reference system (b) and primer modified with containers filled with corrosion inhibitor.

1st level of protection – nanotraps

The first level of protection was provided by the incorporation of nanotraps for corrosive chloride ions and water. To receive information about the trapping mechanism permeability tests of free standing films were performed amongst others. Zn–Al layered double hydroxides (LDHs) intercalated with nitrate anions are suggested as chloride nanotraps for organic polymeric coatings. The addition of such nanotraps to a polymer layer drastically reduces the permeability of corrosive chloride anions through the protective coatings. A coating modified with LDH–NO_3 was found to exhibit significantly lower permeability to chlorides when compared to an unmodified coating, which proves the applicability of LDHs in delaying coating degradation and corrosion initiation [2]. Spectroscopic studies of the absorption of water as a function of the water activity in the environment were performed, which are combined with microbalance experiments in order to get information of the water uptake and the water penetration rate. By the incorporation of water trapping particles in a polymer coating a significant decrease in the water penetration rate through the polymer coating and an increase of the corrosion resistance was observed [3].

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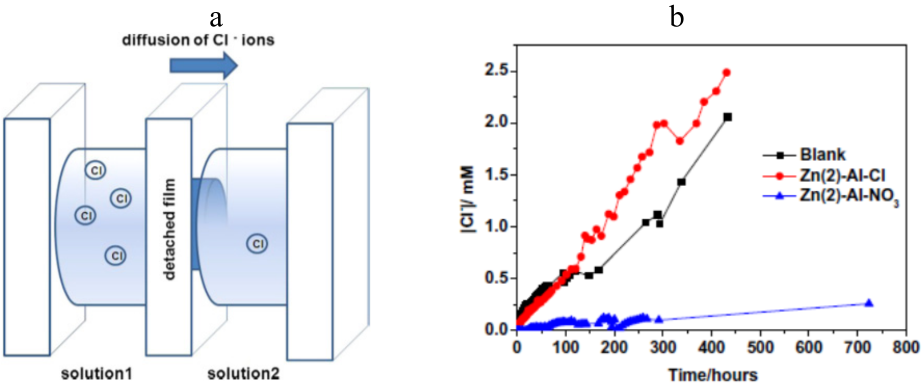

Figure 2. Scheme of permeability tests in a free standing coating (a). Permeability of Cl^- through the coating as a function of time (b).

2nd level of protection – micro-/nanocontainers with water displacing/repelling agents

The second level based on the use of water displacing compounds, which are released from nanocontainers as soon as the first microdefects appear in the polymer matrix. Water repellence was studied by the microscopic analysis of water accumulation within defects. The nanocontainers lead to the release of hydrophobic additives, the local contact angle increases and water repels from the defect areas in small droplets. To analyse this behaviour, a new apparatus was introduced, allowing the study of advancing and receding contact angles during the simultaneous stretch forming of the coated substrate. The incorporation of alkoxysilane loaded polymer capsules into a coating system led to a pronounced hydrophobization of cracks that were formed during the stretching of the sample. The local hydrophobization is assigned to the conversion of alkoxysilanes to polysiloxanes via hydrolysis and condensation which are initiated by the contact of those alkoxysilanes with the aqueous electrolyte during water attack [4].

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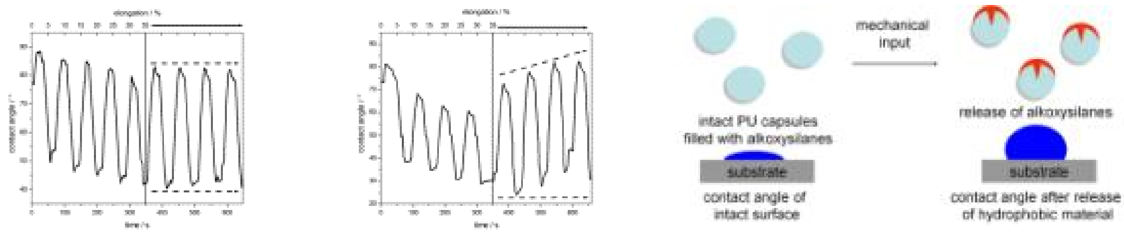

Figure 3. Development of the dynamic contact angle of a coating without capsules (a) and with filled PU capsules (b) during stretch forming. Scheme of hydrophobisation process (c).

3rd level of protection – microcontainers with healing agents and catalyst

For the analysis of self-sealing systems localized methods like local impedance spectroscopy (LEIS) were used to characterize the samples. LEIS measurements of scratched samples containing PU capsules with prepolymer displayed a reduced corrosion activity compared to the unmodified sample. By means of water contact angles measurements during stretch forming the release of prepolymer was shown.

4th level of protection – nanocontainers with corrosion inhibitor

The fourth level of protection is based on encapsulation of organic and inorganic corrosion inhibitors in different types of nanocontainers acting on demand and suppressing corrosion and delamination processes occurring in open defects or at cut edges. Coatings with single nanocontainers were analysed in addition to combinations of nanocontainers and multi-layer coatings. Besides the research of nanocontainers and mechanism of self-healing new experimental methods for testing of the self repair properties were introduced. A multi-electrode was shown to permit the assessment of the corrosion susceptibility and corrosion inhibition of different metals and alloys simultaneously [5]. Ion-selective microelectrodes offer the measurement of the scanning vibrating electrode technique (SVET) with the quasi-simultaneous measurements of pH. These measurements correlate electrochemical oxidation–reduction processes with acid–base chemical equilibriums [6]. The optimization of corrosion protection and self-healing ability of the composite coatings was studied by means of electrochemical techniques. Electrochemical impedance spectroscopy measurements were performed during immersion tests in order to estimate the evolution of the barrier properties and kinetics of corrosion processes. It could be shown, that the incorporation of loaded LDH nanocontainers leads to an improvement of the barrier properties and a drastically reduction of the permeability of corrosive chloride anions. By means of SIET and SVET the local release of the inhibitors was studied. SVET was used both for detecting the anodic and cathodic currents on the metal surface and for studying the inhibitors action on the cathodic and anodic processes. For systems with embedded LDH (MBT) and Cerium molybdate (MBT) an effective inhibition of the corrosion activity was observed [7].

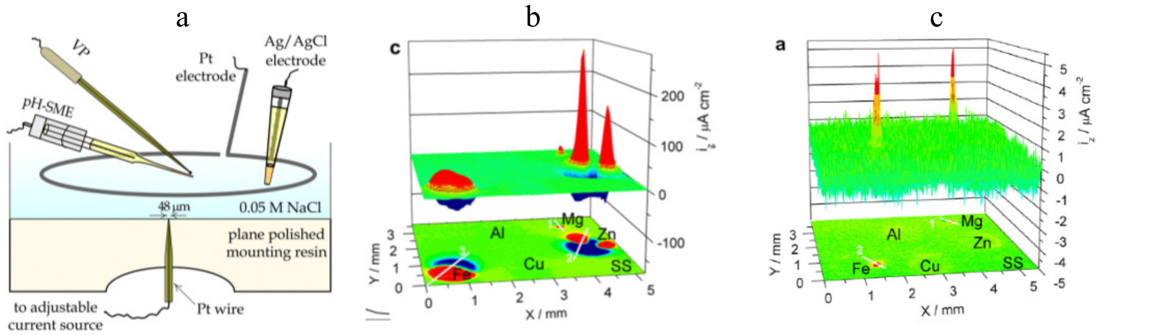

Figure 4. Scheme of the validation cell for quasi-simultaneous SVET-pH measurements (a). SVET map of a multi-electrode cell in a corrosive medium (b) + inhibitor (c).

High resolution Raman Microscopy was applied for the study of corrosion product formation and inhibition in confined microscopic dimensions. TiO_2 nanoparticles were monitored before and after stretch-forming induced defects. Spatially resolved delamination studies were performed by means of the Scanning Kelvin Probe. Thereby, the mechanism and kinetics of de-adhesion were studied. It could be shown, that the loading of halloysites or LDH with MBT leads to a reduction of the delamination rate. In addition measurements regarding the inhibitor release kinetics were performed for LDH.

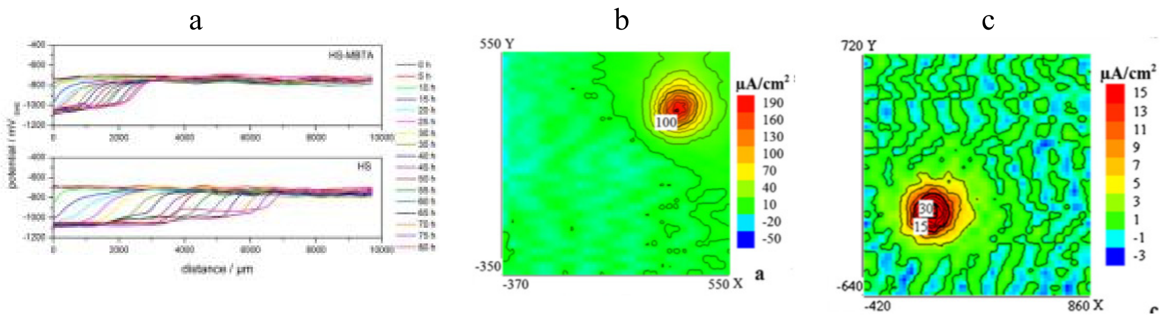

Figure 5. SKP potential profiles of the cathodic delamination of a coating with empty nanocontainers and with filled nanocontainers (a). Current density map of a coating without (b) and with embedded nanocontainers (c) after 18 h of immersion in 0.05 M NaCl.

Overall Conclusions:

The work in SP2 enabled to build a bridge between the nanocontainer design and the resulting properties of coatings and adhesives which were modified by these nanocontainers. Moreover, the fundamental results allowed the advanced simulation of coating properties.

It can be generally be concluded that repair processes and trapping are limited to confined dimensions of several ten micrometres due to the limited amount of functional additives that can be incorporated in the coatings and adhesives.

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WP2-SP3

The main aim of SP3 – "Modelling and simulation" has involved development of effective simulation algorithms, which application allows quantitative description of processes occurring in the multifunctional anticorrosion coatings. Therefore, they can be used to optimise of composition of the coating with respect to contents of the capsules, their distribution in the coating, their surface properties, wetting properties of inhibitors and healing agents, etc. The algorithms were developed basing on the understanding of fundamental processes of formation of containers/particles used at every level of protection as well as their interactions with various layers of coatings or adhesives and mechanisms and rates of release and transport of inhibitor or healing agent.
The following processes were considered:

1. Modelling of the membrane emulsification process to produce cores for encapsulation of hydrophobic anticorrosion agents.
2. Transport of water or corrosive ions (e.g. chlorides) through the multilayer coating that contain water and ion traps and inhibitor pool with built-in various triggering mechanisms.
3. Release of active agent from the core-shell structure (nano- or microcapsule) – diffusion controlled release with permeability controlled by internal trigger (e.g. pH level).
4. Simple and complex simulations of the release of inhibitor or healing agent from capsules in the cracked/scratched coating – i.e. triggering by mechanic damage of the containers;
5. Release of inhibitor or healing agent to the scratch and evaluation of healing effect probability – risk of failure analysis.

The advanced algorithms based on various methodologies as: molecular dynamics, finite differences, Monte Carlo calculations, lattice gas model of diffusion, DPD, were elaborated, software codes were prepared, optimized and verified using the experimental data obtained in other subprojects of the MUST project.

The main achievements of the SP3 subproject are as following.
1. ***Membrane emulsification*** - The model of membrane emulsification based on the balance of forces acting on the drop of the dispersed phase formed at the mouth of the membrane pores were elaborated. The model takes into account process parameters as: viscosity of both dispersed and continuous phase, dynamic interfacial tension, average pore diameter and pore size distribution, membrane structure and wetting properties, temperature trans-membrane pressure and wall shear stress. The effect of hydrodynamic instability during droplet formation and necking was also considered in the model. It was verified first on the simple system of single pore (capillary) and then on the real system of emulsification of hydrophobic liquid inhibitor 2-Methylbenzothiazole as the dispersed phase containing model corrosion inhibitor (MBT). The quantitative agreement between the predicted size of emulsion droplets and measured in the experiments was obtained.

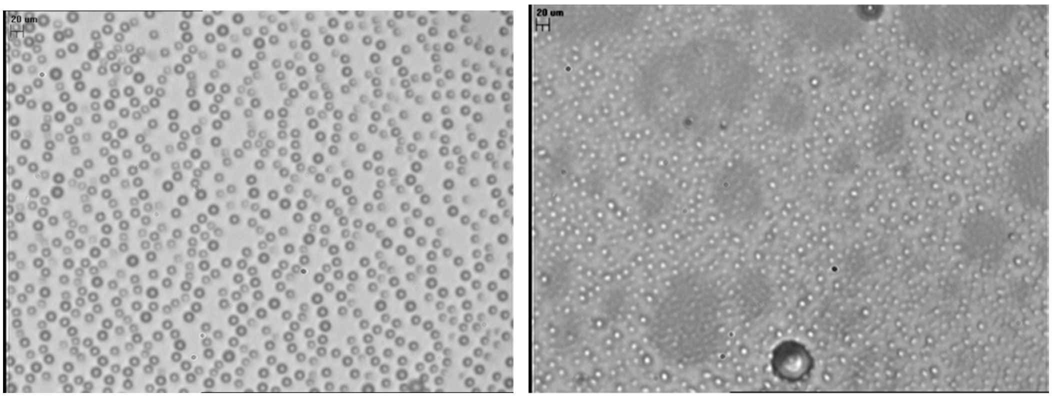


Fig. I. Optical micrographs of 2-Methylbenzothiazole emulsion formed by membrane emulsification method. Predicted size 5.5 μm, 4.7 μm, observed size 6 ± 1μm and 5 ± 1μm respectively.

2. ***Molecular modelling of surface activity of amphiphilic silica sources*** - Molecular structure of surface active species provides information concerning the ratio of the hydrophobic and hydrophilic part of molecules, which allows to predict – using thermodynamic arguments - their surface activity, critical micelle concentration, shape of surface/interfacial tension isotherms. For the modelling, a two stage approach was applied. Quantum mechanics ab-initio calculation and optimization of molecular structure was used to find properties of single surfactants without taking into account explicitly solvent effects. Then the molecular mechanics calculations were used to determine interaction of surfactants with the solvent and to study the conformational effects at interfaces. This methodology was applied determine surfactant properties of DTSACl (Dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride) cationic surface active silica source used in SP1 for the formation of oil drops, which are encapsulated with silica shell due to hydrolysis and condensation of DTSACl. The results of modelling of surface activity were in a good agreement with the observed interfacial properties and allowed optimizing the composition of oil/surfactant/aqueous solution to find the conditions favourable for obtaining stable emulsions. The same methodology was used to model formation of polyelectrolyte membrane by the Layer-by-layer deposition method in order to obtain the correlation between membrane thickness, porosity and permeability.

3. ***Kinetics of release of corrosion inhibitor from capsules –*** Model based on the two step process, transfer of the inhibitor through the oil/water interface (for hydrophobic cores) or dissolution of solid core and diffusion through the shell was developed and the software code based on the final differences integration scheme was prepared. The model was verified with the experimental results concerning the release of fluorescent dye from the hydrophobic core and used to describe the release of corrosion inhibitor (cf. Fig ii).

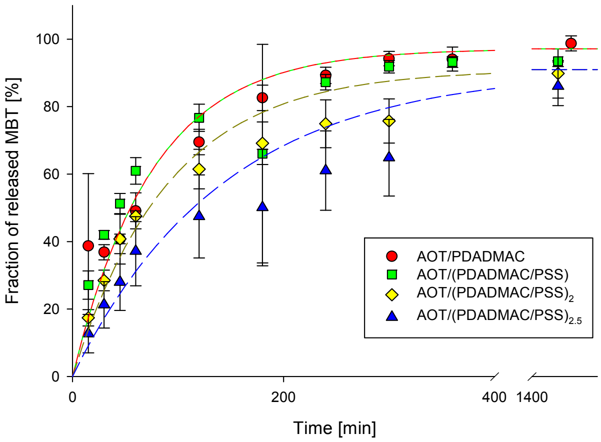


Fig. ii Kinetics of MBT release from nanocapsules with polyelectrolyte shells with various thicknesses. Lines denote predictions of the theoretical model.

4. ***Model of transport of water and ions through the multifunctional coating containing water and ion traps and inhibitor pools*** - The numerical model of multifunctional coating containing water/ion traps and embedded capsules with inhibitor was developed. The alternative algorithms for the solution of diffusion equation in inhomogeneous media, based on the lattice gas model and finite differences were elaborated. Finally the one dimensional diffusion equation describing water (or ions transport) in the effective medium was derived. In the model various triggering mechanisms of the release of inhibitor from containers as concentration thresholds of corrosive ions or corrosion products were considered. Single and multilayer coatings can be simulated with the arbitrary distribution of water, ion traps and inhibitor containers. The model was verified with experimental data obtained in SP2 for:

- diffusion of water through the epoxy film (EU3) containing polymer water traps (SP1);
- diffusion of chloride through the epoxy film containing LDH chloride traps (SP1);
- results for the salt spray test at the EG steel panels painted with a primer layer containing (calcined LDH) (cf. Fig iii).

In all studied cases the quantitative description of experimental results was obtained.

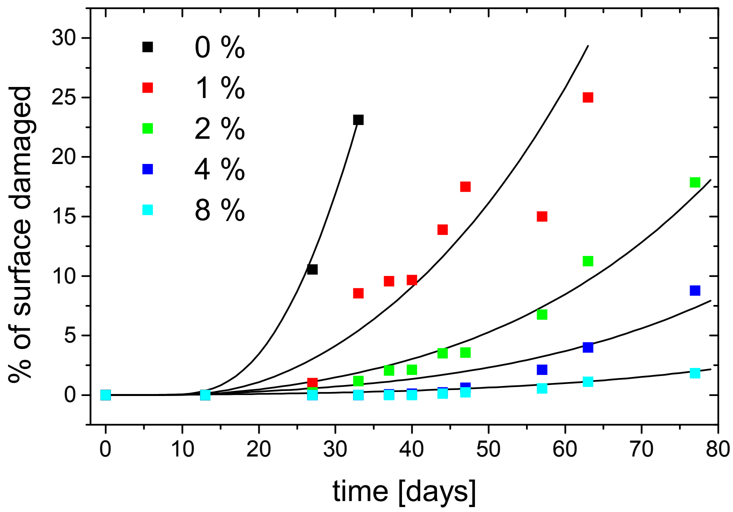


Fig. iii. Percentage of area of surface damaged by corrosion in function of time for films containing different amount of ionic traps. Simulation results are shown as lines.

5. ***Model of the release of inhibitor or healing agent from capsules in the cracked/scratched coating –*** The model based on the geometrical arguments taking into account random distribution of capsules in the film and propagation of the inhibitor either by spreading or diffusion. Two limiting boundary conditions concerning the release mechanism induced by mechanical damage were considered. Either inhibitor is released only from capsules at the edge of the scratch and the material in the scratch volume is lost, or the inhibitor is released from all capsules in the crack/scratch. That simple model was applied to the description of:

- the propagation of hydrophobizing agent, alkoxysilane, from the polyurethane-epoxy capsules in the epoxy coating on aluminium surface;
- release of corrosion inhibitor (MBT) from capsules with polyelectrolyte shells embedded in the epoxy coating (EU3) on the aluminium surface;
- release of prepolymer and healing of the scratch;

In all cases qualitative agreement between the available amount of inhibitor/healing agent and efficiency of coating was observed. That simple model was the starting point to the more elaborate modelling of the active agent propagation in the scratch by the DPD method and finite differences algorithm for the large scale modelling (cf. Fig iv). The latter enables to construct maps of probability of healing the scratch for a given amount of active agent in capsules and volume fraction of capsules in the coating.

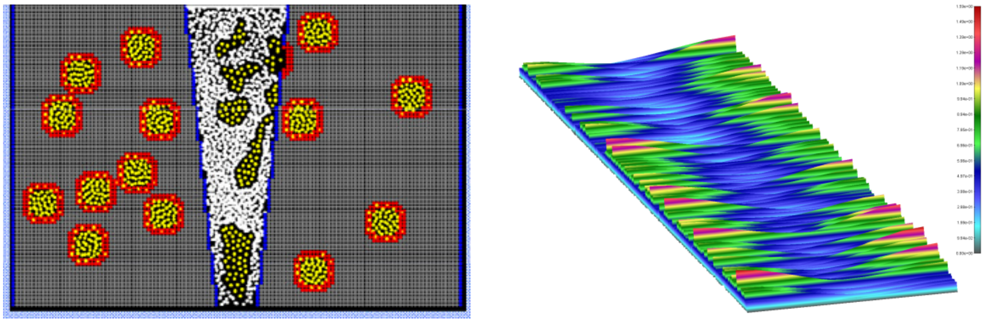


Fig. iv. Propagation of inhibitor into the scratch modelled by DPD and finite diferrence algorithms

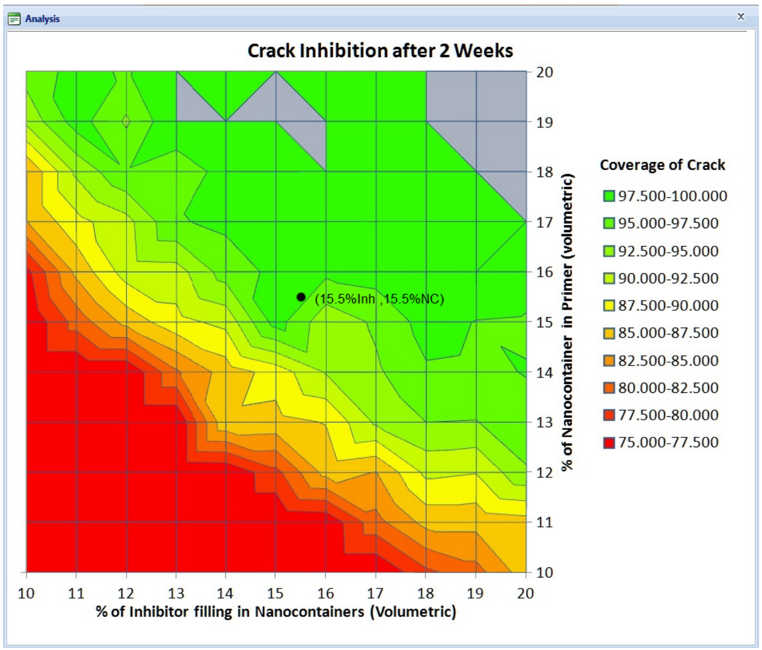


Fig. v. Example of large scale modelling of the efficiency of corrosion inhibition in the crack.

The developed large scale modelling is the supporting tool for technical risk evaluation for the lack of performance of coatings with nanocontainers filled with crack assuming realistic parameters defined by their molecular properties.

WP2-SP4

The objectives for using nanocontainers in coatings and adhesives for automotive applications were mainly to improve corrosion protection in critical areas of the car body. Therefore pre-treatment, primer, e-coat and adhesive were chosen for the development of protective coatings. Novel automotive substrates like pre-coated coil steel were also in focus.

Additionally there was the idea that a new process could lead to a reduction of the complexity and thus to a reduction of cost compared to the current processes. Of course one of the important aspects was compliance with future environmental and legal requirements.

Within the first period of the project model-systems of coatings and adhesives as well as application methods were defined. Metal-substrates to work with (HDG/EA and EG steel panels and Aluminium AC170 + TiZr) and corrosion inhibitors to fill the nanocontainers with were selected. A list of characteristics and requirements for the nanocontainers according to industrial standards was compiled (see 18M MUST report) and updated following the project progress. Samples of the model-systems were provided to the nanocontainer-developing partners.

In a workshop called “Car painting process” and “Cleaning and Pre-treatment”, organized and performed by Chemetall and Daimler AG, PhD-students and further members of the partner institutions got the chance to learn about the industrial processes the nanocontainers should be used for. In March 2011 Sika organized a workshop on adhesives for the MUST partners.

Although the availability of sufficient quantities of nanocontainers was not given until the last year of the project, small amounts of model pre-treatments, primers and adhesives could be doped with a vast variety of first generation nanocontainers and investigated. Throughout all onsets problems with aggregation and sedimentation arose. The experience from these first tests led to requests for a modification of the properties of the next generation of nanocontainers towards the partners developing the latter. And from these experiments LDH-VO_3 nanocontainers from the University of Aveiro and organo-silica capsules loaded with MBTA (SINTEF) crystallized as promising candidates for up-scaling and further investigation.

When eventually larger amounts of a few nanocontainers were available, the problems with aggregation and sedimentation could be worked on. And also big test series with variable formulations could be started.

At first hand promising paint adhesion and corrosion test results were achieved on HDG panels pre-treated with the alkaline model pre-treatment system GTP 10894 containing VO_3-doped Mg-LDH-nanocontainers. In this case the top coat was an architectural paint system. Unfortunately, these promising results could not be shown under automotive test conditions when e-coat was the top layer. The e-coats deposited by Chemetall, Fiat and Daimler on top of the same pre-treatment led to different results in the corrosion tests. From the latest results there is an indication that model pre-treatment GTP 10894 doped with 1%wt Mg-LDH-VO_3 and 0,01%wt free MBTA may lead to an improved corrosion behaviour on EG panels. From the confusing variability of test results emerged a slight suspicion that the up-scaled nanocontainers from BTS do not show the same characteristics as those from the laboratory in Aveiro.

For the evaluation of a nanocontainer-doped corrosion protection primer a method was developed at Chemetall to overcome the agglomeration problem when introducing nanocontainers into the model primer GTP 10892. The nanocontainers were added at an earlier stage of the primer preparation process, which allowed the use of higher dispersing speeds. This procedure led to doped primers with no or only with a very small amount of nanocontainer-aggregates.

From a lot of experiments at first Mg-LDH/MoO_4 nanocontainers were found as most promising for the application in a Shieldex-free model primer system. And also the corrosion protection of water-trap containing Shieldex-free model primer system improved dramatically in the salt spray test with increasing water-trap concentration in the coating.

Unfortunately, these very interesting test results achieved by May 2011 could not be reproduced in the test series following. For each type of test, as there were for example paint adhesion, alkaline resistance, chemical resistance (MEK), Erichsen indentation and neutral salt spray test, one or two GTP 10892-based nanocontainer/primer systems performed well, but there was no primer system that showed good results in two or three or all cases! But still a distinct correlation between the amount of calcined LDH watertraps in the model primer and the protection of corrosion in a neutral salt spray test may be seen.

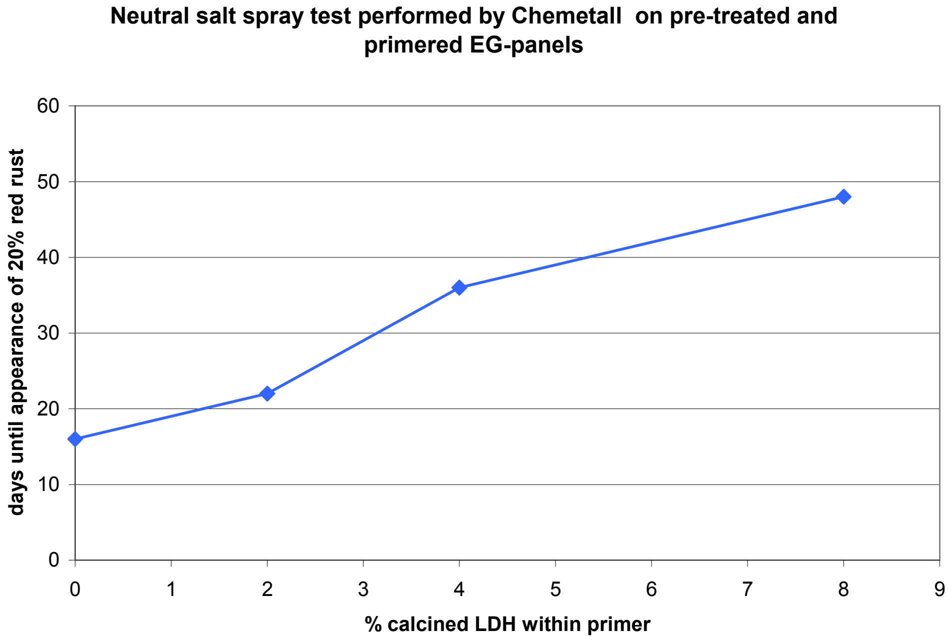


Figure: Results of neutral salt spray test with model primer doped with calcined LDH-watertraps on pre-treated electro-galvanized (EG) steel panels.

Unfortunately the promising results were attained at a very late stage of the project. Nevertheless there still is great believe in the potential of the technology. That is why under the lead of Chemetall the University of Aveiro, EADS, Mankiewicz and Chemetall jointly prepared a patent application concerning the use of very different types of LDH-nanoparticles in pretreatment compositions, passivation compositions, pretreatment/primer compositions, primer compositions, paint compositions and e-coat compositions, especially for corrosion resistance. This patent application was filed on 17 April 2012 in Portugal.

In the work with adhesives the same problems with agglomeration of implemented nanocontainers occurred. But eventually Sika could report that different nanocontainers were implemented into the basic BiW-adhesive without agglomeration by using slurries. According to this, optimal behaviour was achieved with the nanocontainer/epoxy-slurry from MPIKG (nanocontainer: SiO2-MBT). Very good agglomeration free incorporation was also possible with the nanocontainers developed by UAVR and up-scaled by BTS (e.g. MUST 2011-16; MgAl-MBT). The problem with the latter was that they were received as a nanocontainer/solvent-slurry. This implied a time-consuming preparation of the adhesive, because the solvent had to be evaporated out of the epoxy/nanocontainer-slurry. Furthermore the CeMo-MBT nanocontainers from NCSR could even be implemented with little agglomeration without creating a slurry.

The corrosion resistance compared to the basic adhesive was significantly improved by several nanocontainer-doped adhesives on an aluminium substrate. On steel only a slight improvement regarding corrosion was observable with a few nanocontainer-doped adhesives. Unfortunately these promising results emerged at a very late stage of the project as well.

As after the beginning of the project the decision was taken to substitute the work with powder coatings by work with e-coat material, between CRF, Varnish and Chemetall a proposal for planning and building a laboratory plant for pre-treatment and e-coat activities at the CRF laboratories in order to test and compare different processes was created. After the approval of the project consortium Varnish started to design, construct and actuate the plant at its premises and finally delivered it to CRF. During the run-up quite some modifications had to be made until satisfying e-coated panels could be obtained.

Figure: Laboratory e-coat plant established within MUST project.

For the qualification of the pilot line a commercial e-coat system as well as a model e-coat system were used. After that evaluation the effect of nanocontainers within e-coat material should be examined. CRF made contact with BASF in order to decide on the best model e-coat system for their doping tests with nanocontainers. A list of nanocontainers was tried out and again there were problems with aggregation and sedimentation. Samples of the e-coat system were provided to the SP1 partners to improve compatibility.
Eventually panels were prepared with nanocontainer-filled e-coat layers. The proof that nanocontainers are deposited on the panel surfaces is pending. The corrosion test results of various combinations of doped/undoped e-coat and doped/undoped pre-treatment layers are also pending.

All deliverables planned for the subproject in the first period of the MUST project could be submitted in time. The deliverables planned for the final stage of the project had to be modified, if not cancelled at all. The key issue that could not be tackled is the compatibility and performance of the developed promising nanocontainers with commercial coating and adhesive systems.

WP2-SP5

Due to the lack of suitable alternative inhibiting pigments for the replacement of chromates new inhibition concepts are required for aerospace coatings. The encapsulation of inhibiting substances is one approach to achieve sufficient effectiveness of inhibition also for long term protection purposes. The advantages are e.g.:

- Bigger choice of inhibitor candidates and combination thereof can be used because of better compatibility with matrix
- Smart and triggered release is enabled by encapsulation and controls inhibition process

- Increased inhibitor concentration can be obtained

During the project different paint matrices were investigated for their suitability of incorporation of nanaocontainers. The selected paint system is in accordance to aerospace standards and will contain selected nanaocontainers. During the screening phase only AA2024 unclad was investigated since it allowed a high differentiation of performance between protection systems. Later on in the demonstration phase materials such as AA2024 clad and AlLi alloys are introduced. Chromic sulphuric acid pickling for screening purposes and in the later project phase a chromate free anodising treatment, the tartaric sulphuric acid anodising (TSA) was used. TSA is a new qualified chromate free aerospace pretreatment for painting applications on aerospace aluminium structures.

The development of the Model Film has been carried out by Mankiewicz in several steps. Starting with the Model Film EU01 the barrier properties of the films had been increased from Model Film EU01 < EU02 < EU03. Electrochemical impedance measurements (Figure 1X.) and salt spray test helped to identify the most suitable system (EU03A) with the highest barrier as a model film. Also in salt spray test the film EU03A showed a slight better performance than EU03B. No corrosion occurred after 336 h exposure to salt spray on a pickled AA2024 unclad substrate.

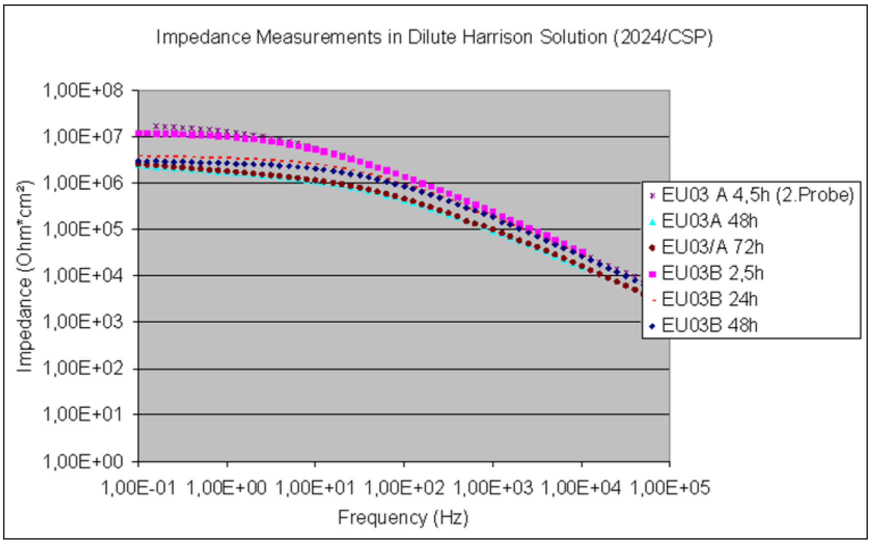


Figure 1: Electrochemical impedance of two versions of model film

The introduction of nanocontainers was performed at Mankiewicz. The dispersion of different containers into model film and model primer was successfully established by using water borne container suspensions. Macroscopically, coatings look homogeneous without any agglomeration. The incorporation of nanocontainers could be established as a standard procedure.

The following systems could be integrated in the model film and the model primer and corrosion performance could be carried out:

- Polyelectrolyte shell
- Mesoporous silica
- Layered double hydroxide LDH
- Halloysites
- TiO2 nanoparticles

Several approaches were investigated for dispersing the nanocontainers properly and producing satisfying films. Finally a valid procedure could be specified to produce the coating system. Approximately 200 different combinations of film/container/inhibitor/pretreatment systems have been selected and applied for testing. The following aerospace relevant tests were performed with the coatings:

- Paint adhesion test before and after water exposure
- Scratch resistance before and after water exposure and after exposure to hydraulic fluid
- Flexibility testing
- Drop Test for evaluation of corrosion protection of mechanical defects according to a test developed within MUST
- Salt spray test according to EN ISO 9227 for evaluation of scratch corrosion protection, protection against paint creepage and barrier properties
- Filiform corrosion test (for selected systems) according to EN ISO 3665 for evaluation of filiform corrosion resistance
- Alternate Immersion and Emersion test (for selected systems) for evaluation of leaching behaviour, corrosion protection of mechanical defects, protection against paint creepage and barrier properties. Some of the promising systems were also analysed in SP2 for basic understanding of the performance and mechanistic investigation (inhibition effect, barrier properties)

Corrosion on coupon level

In general it can be stated that the corrosion inhibition of exposed surfaces as tested by the drop test is not achieved by any inhibitor loaded system. This can be attributed either to the concentration, to the efficiency or the leaching behavior of the corrosion inhibitors.

Often the coating barrier is lowered by the integration of the containers. Low adhesion after water exposure or blistering in salt spray test is often the consequence. Nevertheless during the development work in the project it was possible to optimise the systems and to accomplish these problems.

Some differentiation between the systems can be made on the basis of longer term test such as salt spray test for 1000 h and filiform corrosion test for 1000 h where paint creepage is detected and rated according to the depth.

A differentiation between the combination of capsules with dummy primer and model film EU03 has been done on CSP treated AA2024 unclad. Since blistering was an issue on CSP treated surfaces further evaluation on best candidates is performed on tartaric sulphuric anodised surfaces (TSA). The figures below show that the encapsulated systems before upscaling camping provide better corrosion protection than the commercial system without chromate (**Figure-2**). Unfortunately after upscaling these clear benefit were not confirmed (**Figure-3**) and that the performance of the CrVI loaded systems cannot be achieved.

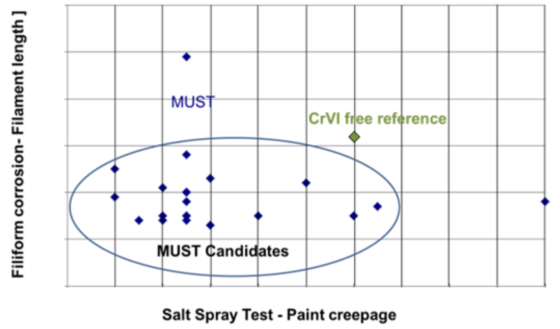


Figure-2: MUST systems before upscaling on TSA in long term corrosion test

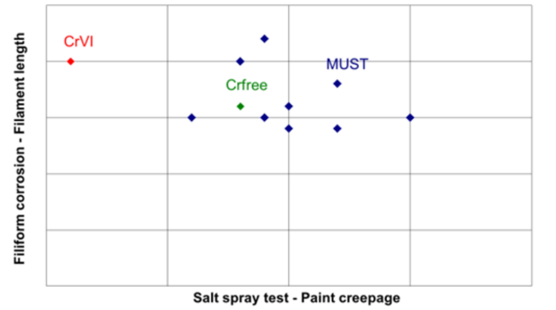


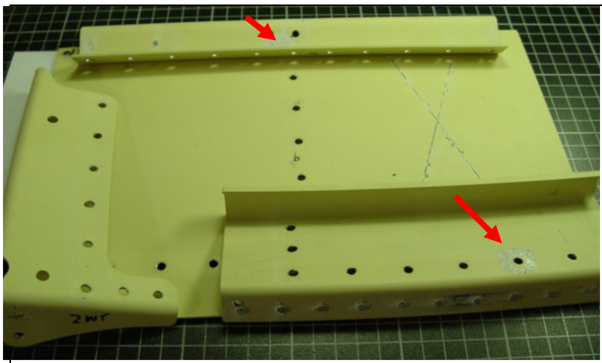
Figure-3: MUST systems from upscaling applied on TSA in long term corrosion test

All MUST systems show a positive behaviour in both corrosion tests. However, in salt spray test they cannot reach the performance level of the CrVI loaded primer. In filiform test some systems perform even better than the standard system. Yet, they compete with the commercially available CrVI free primer. A clear benefit of the containers is not observed in these tests.

Corrosion testing on demonstrator level

Specific design elements were to be selected which are representative for the certain areas of the aircraft structure. The demonstrator was to be defined with respect to the respective manufacturing process of the structure and the potential application process of the coating. The design of the demonstrator should reflect realistic but also challenging condition for the protection system and must also consider the existing requirements of the different testing and evaluation methods. With regard to availability, quality, reproducibility, performance and mechanistic understanding several encapsulations systems were prepared based on LDH-Inhib1, LDH-Inhib2, Halloysite-Inhib3, Polyelectrolyte-Inhib2 and compared with CrVI-free and CrVI-loaded reference systems.

Corrosion tests with demonstrators revealed the relevant corrosion hot spots: Paint creepages at defects, blistering on surfaces, galvanic corrosion, crevice corrosion. The chromate loaded reference systems inhibit these corrosion hot spots successfully over the test time. The MUST systems and the CrVI free reference primer allow these hot spots nearly to a similar degree to occur. A clear benefit of one of the MUST systems is not observed



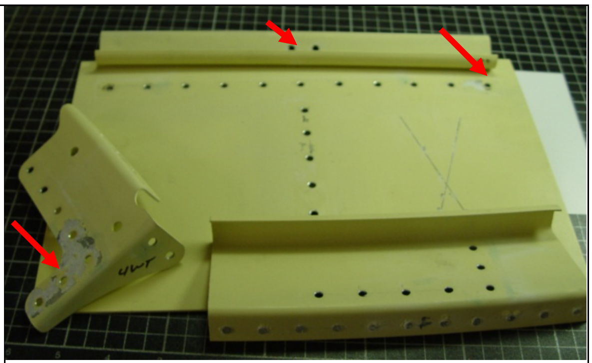


Figure-4: Corrosion Test on demonstrator in Salt Spray test after disassembling	Figure-5: Corrosion Test on demonstrator in Salt Spray test after disassembling

Aerospace relevant tests were performed by EADS and revealed that the benefit of the introduction of nanocontainers lies in the long term protection rather than in the short term protection of mechanical defects. In filiform corrosion and salt spray test the added on effect by nanocontainers is visible whereas the upscaling procedure still has to be improved in order to exploit the benefits of the encapsulation approach.

WP2-SP6

The main objective of SP6 is the development of new multi-level protective coatings based on active nanocontainers for maritime applications. The currently used maritime coating formulations are modified by doping them with appropriate nano-/micro containers developed by SP1-partners in the MUST project. The objective as well as results of this particular work package is described in the following.

The substrate to be coated is defined, and the main candidate is mild steel which still is a main structural material for maritime applications. The coating formulations are selected from epoxy based systems currently employed for ships. The requirements for potential micro-/nano-containers are formulated from standpoint of compatibility with paint formulations in order to be used by SP1-partners during design of new active nanoreservoirs.

The water or solvent based suspensions or nanopowders of functional nanocontainers developed by SP1-partners are added to the selected paint formulations and the resistance of obtained paint formulations against aggregation and sedimentation of pigment is tested. The first level of protection is achieved by introduction of nanocontainers with corrosion inhibitors. In addition nanocontainers doped with biocides to achieve anti-fouling properties have been introduced.

The corrosion protection performance and other important properties like scratch resistance and adhesion is tested according to the following standards:

- Corrosion protective properties - ISO 12944-5
- Film thickness - ISO 19840
- Roughness - ISO 8503
- Adhesion - ISO 4624

In addition, the wetting properties (contact angle measurements) of the solvent-based two-component marine coating (Green Ocean Coating GOC^{TM}) is characterized and the surface topography (white-light interference) defined. Innovative inorganic organic hybrid particles are synthesized by functionalization with fluorinated units and incorporated into the hardener component in order to increase the hydrophobicity of the epoxy paint (unmodified reference: contact angle $\Theta = 70°$) and thus to reduce the friction properties of these coatings in maritime applications. The information on wetting properties of modified coatings against water has been extended to the possible parameters of different temperature during wetting, including seawater as test liquid and tilting method to determine the rolling resistance of a liquid (friction).

The two types of specifically functionalized inorganic organic hybrid polymers (FunzioNano^{TM}: RT-1 and RT-2) developed at SINTEF showed to be suitable to decrease the wetting properties of the epoxy coating against water. Both types of hydrophobic functionalized FunzioNano^{TM} have been used for modification of GOC^{TM} coating in different concentration levels (1wt%, 2wt%, 3wt%, 5wt%, 10wt%; calculated to cured epoxy resin) to evaluate maximum hydrophobic surface properties of the modified GOC^{TM} coating films. Increasing the concentration level of RT1 nanoparticles for modification of GOC^{TM} epoxy formulations seems to also further increase the contact angle against water.

An addition of 10wt% RT-1 led to a contact angle difference of almost $\Delta\Theta \sim 20°$ related to the unmodified coating. This means RT-1 is suitable to improve significantly the hydrophobic surface quality of the GOC^{TM} -HeavyDuty system resulting in a contact angle of $\Theta = 115°$ and can be competitive with the benchmarks Intersleek700^{TM} and Sea Quantum^{TM}. Whereas the commercial coating products seem to obtain their hydrophobic surface qualities by a certain micro-roughness, the GOC^{TM} specifications using the RT1-type modified hardener give hydrophobic material properties due to their chemical modifications – the surface is very smooth. Variations in the concentration level of RT2 nanoparticles in the marine coating film did not have such a strong influence on the wetting properties of the modified coating.

An up-scaled version of RT1-type GOC^{TM} coating prepared at SINTEF has been applied by spray coating at site (Re-Turn) in mid of March 2009 for tests under realistic conditions (towing tank testing based on measuring hydrodynamic friction forces) in South-Africa. The results from samples prepared under real conditions at site in large scale (spray application) show that a difference of surface qualities might be achieved compared to lab applications. Main emphasize has to be given to the maintenance of spray equipment in order to achieve and to reproduce high quality surface qualities attributed to special materials properties designed in GOC^{TM} -Red-1 formulations.

Anti-corrosion

In order to test how nano/micro containers doped with anti-corrosion inhibitors can be dispersed into the selected maritime epoxy coating, complete samples of the coating systems is send to six SP1 partners for them to test and describe how this successfully can be done. Each of the partners has received both a water borne epoxy system and a solvent free epoxy system complete with hardener. Each SP1 partner has doped the nano/micro containers with their best working anti-corrosion inhibitors and dispersed them into the epoxy system. The complete system is tested for anti-corrosion properties in salt spray chamber where after the best candidate is chosen for large scale testing and demonstration in the WP3 project phase. Testing of panels for anti-corrosion properties is done both according to 'ASTM B-117/ISO 9227 – Corrosion testing in salt spray' and 'ISO 2812 - Determination of resistance to liquids'. All together it is prepared 280 test specimens to test 18 different systems in various environments. The selected candidate from these tests is halloysite-based nano containers from Max Plank loaded with the corrosion inhibitor 1H-benzotriazole in two different ways.

Anti-fouling

To test and select the most promising coating system with nanocontainers doped with biocides for anti-fouling properties test specimens are submerged in seawater for prolonged periods at test stations in Norway and in Singapore. Preliminary results from testing maritime coating system with CuO nano containers doped with biocides are showing promising development. But as the samples being tested only has been immersed in sea water for a few months it is too early to judge whether they will continue to develop in a positive manner, and if they will show better results than traditional epoxy systems with copper and biocides. As there is no way to accelerate anti-fouling tests to get quick results the tests will continue for a prolonged period to see if the nano-system outperforms service-life of standard system which is five years.

WP4

Objectives
The dissemination strategy of MUST envisaged at reaching a broad range of audiences, including the scientific and industrial communities, the general public and the key decision makers – Figure 1. All the partners have been encouraged to be involved in the dissemination activities. Specifically, the partners were committed to present the project results in conferences, info-days and other dissemination events; to participate in workshops, to prepare scientific papers for conference presentations or journals, to contribute for the web-site contents, to be involved in training and formation of researchers and to highlight the project results.

Key activities developed:

Electronic dissemination
The MUST web portal (www.sintef.no/Projectweb/MUST) highlights the project objectives, achievements and relevant events that were organized. In addition to this portal, several partners have created advertisements in the web pages of their institutions, thus creating additional branches for the project dissemination. Targeted to a large array of audiences, with a high visual impact and a clear and concise language, the MUST video, will increase the awareness of the project.
The research partners participating in the project were selected on the basis of their excellence in particular areas, providing complementarities of expertise and skills needed for the successful project realization. The R&D institutions are also excellent in terms of publication of scientific work. Therefore an outstanding number scientific publications reporting the project achievements was prepared and published in journals of high scientific impact. Figure 2 depicts the final figures concerning this point. The total number of publications was above 100 during the project lifetime and several are expected after the project. Such number of publications is a clear confirmation of the excellent R&D work developed within the project.

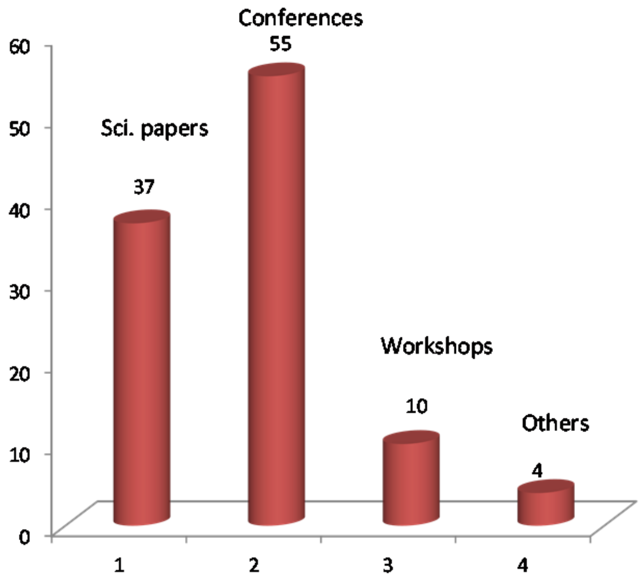


Figure 2 – Scientific achievements of MUST

In addition MUST partners have presented the project in Info days; EUCAR meetings Fumat Conference, EuMAT, etc.

To strength the networking activities MUST organized 4 workshops as listed below.

- MUST - Multiprotect workshop focused in the dissemination of MUST objectives and aims and creation of the first layer of networking industrial partners.
- Must second Workshop was organized in conjunction with a large coatings conference (COSI)
- Life cycle assessment (LCA) & risk analysis in nanomaterials-related NMP projects
- Must Final Workshop focused in the MUST achievements and broadening of MUST strategy towards different materials.

Education and training

Mobility of researchers, at the doctoral and post-doctoral level has been implemented in MUST. This strategy contributed for educating and training high-level researchers, more capable of contributing effectively for the implementation of the R&D and technical activities developed in MUST, supporting the EU research effort.

Six training courses were organized within MUST, both by the R&D and industrial partners:

1. Electrochemical Impedance Spectroscopy, Lisbon , November 6-7 (MUST & MULTIPROTECT) – IST + UAVR
2. Cleaning and Pre-treatment technology , March 9-10 – IST + CHEMETALL
3. Risk analysis – IST + STEINBEIS R-TECH , March 11, 2009
4. LbL of nanocontainers – IST + MPI, October 15-16
5. Adhesion and related characterization techniques, University of Paderborn, September 2010.
6. Adhesives and its testing - SIKA AG Zurich March 16-17 2011.

A total of 19 PhD students (5 PhD theses completed), 7 MSc students (5 Msc thesis completed) and 13 post doc students worked for MUST. Thus, MUST actively contributed to the education, formation and training of early stage researchers, thus strengthening the human R&D potential within EU.

Recommendations and guidelines
EADS and Chemetall created datapools for collecting all the data gathered in the various tests performed on aeronautic and automotive materials, respectively.

R-Tech created a database repository for SDSes (safety data sheets) in ENM. Currently, there are 157 SDS stored in the database. SDSes of the nanocontainers were requested from the project partners. In addition, MUST WP3 meeting in Leverkusen identified the nanocontainers required for the database. SDSes in the database are classified into 5 categories: Nanocontainers from the MUST project partners (9), Primary nanomaterials from the external sources, Functionalized nanomaterials from the external sources, Products contained nanomaterials and other.

Patents
The MUST exploitation strategy was successfully represented in 5 patent applications: Preliminary patent application (Nr. 106256): "Process for coating metallic surfaces with coating compositions containing particles of a layered double hydroxide", M.G.S. Ferreira, M. Zheludkevich, J. Tedim, V. Gandubert, T. Schmidt-Hansberg, T. Hack, S. Nixon, D. Raps, D. Becker, S. Schröder, Universidade de Aveiro, Chemetall GmbH, EADS Deutschland GmbH and Mankiewicz Gebr. & Co. GmbH & Co. KG.

In addition two patent applications were submitted by MPI on the fabrication of nanocontainers and R TECH prepared a patent on modelling system is under the patenting process. NCSR placed an abstract for a future patent application, too.

Business creation and new jobs
An SME – SMALLMATEK (www.smt.pt) was created during MUST and its business activities are very much focused on nanomaterials production for improved durability of coated materials. This SME created two full time equivalent jobs.

In addition MUST has created new jobs (at least two), by hiring 2 researchers to work at full time in the project development.

Exploitation plan
Preliminary exploitation plan was developed and delivered (18M). Basis for the development of the preliminary exploitation plan were implementation plan according to CORDIS guidelines and the Exploitation Strategy Seminar by Mauro Caocci, CIMATEC, ESS Coordinator. The preliminary exploitation plan identified the results with exploitation potential of the MUST project. The plan was continuously updated. R-TECH launched 2 surveys to collect and analyse interests, data and ideas concerning the possibilities for further deployment and exploitation of the MUST project outcomes.

R-Tech web based Survey tool is accessible through the Member Area of the R-Tech MUST web page (http://must.risk-technologies.com). Survey tool allows a creation of fully customizable surveys, conducting the surveys and evaluating the results. The survey had two steps. In the first step the project partners identified exploitable results which are of interest for their

company/organization. In the second step, the partners answered questions only for selected exploitable result(s). All questions ware organized in the user friendly way (yes-no and multiple choice answers). However, it was foreseen also possibilities for the comments, if needed. Each partner has got personalized link, intended only for one partner.
Results were evaluated at the consortium level and by each partner.

Key findings of exploitation surveys: Exploitation plan at consortium level

1. **From 37 exploitable results as most desired for exploitation indicated:**

- Testing equipment and methods: Surface and electrochemical characterization (13 p)
- Nanocontainers with inhibitors (13 p)
- Nanotraps (13 p)
- Nanocontainers with water displacing /repelling agents (12 p)
- Pre-treatment and primer formulations Automotive applications (11)
- Self-healing anticorrosion coating systems for automotive application (10 p)
- Formulation for nanocontainer - based coating systems Aerospace application (10 p

2. **Time to market**

Despite the fact that in some cases additional development and validation work will still have to be done, some of the new technologies may already be implemented within 12-18 months after the termination of the project. Expected time frame for commercial exploitation - Average: 3 years

3. **Foreseeable markets and estimation of competitors**

- NC production and applications have small markets (mostly 1-5 competitors)
- For formulation for nanocontainer – based adhesive systems: competitors Dow Automotive, Henkel, EFTEC, Lord
- Application markets often have no competitors with nanocontainer technology
- Market size is generally “medium” for production and applications
- Methods and testing have competitors in top EU universities

4. **Intended exploitation (exploitation claims)**

- Production and commercialization: 59.5% exploitable results
- Internal use: 78.3% exploitable results
- License to 3rd parties: 35.1% exploitable results
- Provide services: 35.1% exploitable results

5. **IPR Issues**

IPR issues are regulated in MUST project in the following way:

- Joint ownership of foreground makes sense if the more beneficiaries have contributed to the foreground
- According to CA/GA of MUST the situation is quite flexible and simple at the moment: Each of the joint owners can use foreground without obtaining consent of other owners as long as not otherwise agreed.
- Just:
  Notification has to be made about licensing
  Objection to licensing is possible within 4 week

6. Non-commercial Exploitation

- The promising results obtained during MUST will prompt further R&D activities in small, bilateral collaborations with some of MUST industrial partners towards development of systems for commercialization
- Further R&D in the field of systems/plants for surface pre-treatment and treatment
- Improvement of current coating systems and surface treatments to improve long term performance
- Further R&D test: transfer nanocontainers for other applications and systems
- Application of Nanocontainer Know -how to new formulation of coating systems
- Application of Nanocontainer Know-how to new functionalities of coating systems (Multifunctionalty)
- Further fundamental research on the functionality of additive filled nanocotainers in thin films
- By publishing high-quality papers about the MUST results, academic partners will obtain improved international visibility and improve their position
- Finally, it is foreseen that universities and research institutes will exploit the results by integrating them into their educational and training programmes, allowing more and better qualified engineers completing their master and PhD programmes
- Within MUST project 5 PhD Thesis and 5 Msc Thesis are completed 15 mobility tracks for students (Msc and PhD) betwen partners report

7. Patents and recommendations

- Part of the research and development work performed in MUST was incorporated directly in patents and recommendations.

8. New business opportunities

- University of Aveiro has created a spin-off company Smallmatek, Small Materials and Technologies, Lda (www.smallmatek.pt). This is a R&D Company that provides consultancy services and products in the field of coating technology, corrosion and nanocontainers. The main activity is monitoring, characterization and development of coatings for corrosion protection, using new and innovative nanotechnology solutions, including controlled release of active species from micro and nanocontainers. Some of the products may include LDH nanocontainers. This is probably a good vehicle to maximize the application of developed materials, processes and applications related to LDH systems.
- Contractually regulated collaboration between University of Aveiro and Chemetall GmbH

9. Possible new applications of MUST results

The Multi-level protection approach and MUST solutions will also open new opportunities for the application such as:

- Knowledge and contacts on incorporation of nanocontainers in adhesive formulations
- The topic of controlled release of active species from LDHs is promising for applications in other fields of coating technology and structural materials.
- Introduction on NC for other functionalities like erosion protection, self-cleaning, anti-icing.
- Application of MUST solutions for self-healing in damage protection of bulk materials.
- Further development in medicine, self-healing etc
- The coil coating lines, systems for temporary corrosion protection and primers are potential systems for the implementation of solutions boosted by the MUST achievements.

- Some partners involved in project proposals concerned with the application of Nanocapsules in the building field (cement production)

10. Exploitation Risks

Technological risks

- Lack of quality control of the NC production
- No reproducible results
- NC size is too high due to aggregates
- No stable dispersions
- Non homogeneous pre-treatment layer on the test panels
- Functionality for any commercial product is not proven yet for any system
- Outstanding demonstrator result
- Improvement of processing for up-scaling - Analysis of causes for scattering of performance - Reduction
- The scale up is still a limitation for some products
- Application process of self-healing products has still to be investigated and tested
- No obstacles are forecasted in the design and production of self-healing products applications systems.

Market risks

- Rapid drop of the coating market
- Existence of several worldwide suppliers of LDH materials for generic applications
- Potential costs associated with scale up of production of nanocontainers
- to find investors to support the exploitation at industrial scale
- to develop the market (the companies within MUST)

Partnership risks

- Protection of the technology
- Complex patent situation

Conclusion / remarks

Now that MUST project has ended, it can be concluded that MUST was very successful. Certain know-how, products, processes and tools developed in the MUST project have a high potential for future exploitation and usage in different applications for public (non-commercial) as well as commercial use. For example, the promising results are:

- successful development of pre-treatments and primers
- e-coat and adhesives modified with smart additives for improved durability
- Nanocontainers and nanotraps for all four levels of protection are developed
- The concept of different healing mechanisms is proven in model coating systems
- Different level of technology readiness is achieved in the case various nanocontainers
- The synthesis of most promising nanocontainers are up scaled to 30 L batch without loss of performance
- Modelling
- Tools for risk assessment

The adequate exploitation activities will be carried out by the individual partners in such ways as they see fit and in accordance to the terms and conditions under which such activities may be performed

Relevant factors that set the basis for a good exploitation of MUST results are:

- Cooperation among strategic partners with complementary business role
- Experimental validation in lab trials, in order to get early feedback at the research stage
- Patent Applications in order to protect the innovative produced knowledge.

To maximize the exploitation high value was set on the following action points:

- Exploitation-oriented upgrade of the official MUST project website and partner web sites
  http://www.sintef.no/Projectweb/MUST
  http://must.risk-technologies.com
- Publishing of the MUST methodology and solutions in order to lay the foundation of potential commercial projects
- Participation at conferences, exhibitions, fairs and workshops, where the results of the project could be presented to business stakeholders and contacts for potential commercial projects could be built. 106 publications, 37 scientific publications, 55 conferences, 10 workshops
- It is foreseen that universities and research institutes will exploit the results by integrating them into their educational and training programs, allowing more and better qualified engineers completing their master and PhD programs
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As documented above, the focus of MUST was predominantly on research, development, validation, verification, and implementation of technology and technology concepts which can be produced and deployed at a European and global level. Most MUST deliverables are in the public domain. The technologies and concepts developed were published and will be patented. The research carried out in MUST generate considerable output which was put forward to industry groups. Further development efforts can therefore be pointed into a single direction instead of multiple directions, allowing more efficient use of resources, dissemination of foreground quicker time to market.

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The Multi-level protection approach and MUST solutions will also open new opportunities for the application.

The impact of exploitation of the MUST results produced is very difficult to quantify or even to estimate in quantitative terms. Looking at the dissemination efforts and industry feedback which the project received throughout its lifespan and final workshop, it is likely that effects of its work will emerge across the whole of the European industry.

As a conclusion, it can be stated that the valorisation and exploitation activities carried out throughout the MUST project have been planned from the start, ensuring in this way that the partnership was able to carry out all the envisaged activities in due time, and the results are very positive, since the project has reached people and institutions from all the Europe.

Concluding statements
A network of industrial partners was created around MUST, leading to closer discussions between MUST consortium and those interested external companies.

New application fields for the MUST concept were discussed and emerged as potential future exploiters after dedicated R&D and technical work.

MUST became part of the "vocabulary" in anti-corrosion smart coatings both at R&D and Industrial levels and most of these players are aware of MUST achievements. MUST is now the most well-known project in the research field of coatings for metallic substrates.

MUST is reaching all target audiences: industry, R&D players, key decision makers, and general public.

Potential impact, main dissemination activities and exploitation of the results

1. Socio-economic impact and the wider societal implications of the project

The coating materials and materials systems that were developed in MUST are based on smart properties like controlled release on demand of inhibiting compounds and self-healing function reacting to different levels environmental excitation. These protection systems will provide for more sustainable components and give the chance for decreasing cost by reducing process steps during pre-treatment and in the paint shop independently of the specific type of transport industry. The results of the MUST project will directly enhance the economic success and competitiveness of industry. An additional indirect effect on competitiveness could be obtained through improvement of the environmental situation by saving energy consumption in the surface pre-treatment and painting processes and avoidance of hazardous compounds in the used materials and applied processes.

The results from MUST will contribute to improve the competitiveness of the European transport industries as summarized below:

- Effective and environmental friendly protective coatings for transport industry are available in sufficient time to fulfil existing and projected European, US American environmental regulations, thereby increase the sales of the coating suppliers and enhance the global market attractiveness of the vehicles.

- Lower weight of the coating system and higher amount of implementation of light weight substrates will further reduce operational costs by fuel consumption savings and decrease CO_2 emissions.

- The multi-level approach will decrease production costs by reducing process steps during pre-treatment and the paint shop. There is also the potential for simpler and faster processes, lower amount of waste and facilitation of multi material treatment. Depending on the complexity of the protection scheme to be replaced, the manufacturing cost for the coating application can be considerably reduced up utilizing micro- and nanocontainers with reasonable costs.

- The increased application of improved long term stable adhesives to the body in white will enhance the passive safety by increase the fatigue stability, stiffness and the crash performance.

- The application of self-healing and long-term sustainable protection system offers the chance to increase service life of the futures vehicles. Improved sustainability will reduce maintenance cost by fewer amounts of repair charges and extended inspection intervals in service. Reduction on maintenance costs of 20-30% per vehicle is achievable.

One important advantage of the nanocontainer approach is that the development cycle of the advanced systems can be managed to be relatively short, since the containers can be implemented in current, available and experienced matrix systems for new design or for repair systems. The compatibility with presently used substrates, pre-treatments and other components of the protection concepts is expected to be very high. This is generally very important for aerospace industry where introduction of new systems is connected with long lasting and expensive certification and qualification procedures. The time to market/application can be estimated to more than 50% shorter than for a new matrix system.

Another benefit is that the results of the MUST project could also be transferred to other multifunctional protection approaches by combination of the MUST solutions with other functions like superhydrophobicity, sensing properties (impact detection, fluorescence, etc.), anti-contamination and anti-erosion.

MUST has focused on the development of effective environmental-friendly multi-level active protection systems for materials used in future vehicles. MUST will therefore contribute in increasing considerably the life cycle of these materials and therefore boost the competitive strength of the European transport industry. The multilevel protection approach can also open possibility for the application of new light materials (magnesium and aluminium alloys) in vehicle manufacturing. In the sector of nanocontainers, the activities have just started and the high innovation potential of this project will make the members of the consortium and the linked industry most competitive at international level.

The final results are expected to have a positive impact on the environment as HSE regulations have become an increasing challenge for transport vehicle manufacturers, especially in the field of corrosion protection where currently applied outperforming coating systems still contain hazardous compounds like chromates, nickel and cadmium. Replacements for such substances are in many cases less effective and will increase process and maintenance costs. New strategies for protection systems like the incorporation of nanocontainers have high potential to avoid the environmental impact, provide similar effectiveness of protection and can be applied in a reasonable time scale of 4-5 years. The multi-level approach with smart release and self-healing functionalities will open the door for new production concepts with reduced process steps, lower consumption of energy and conserving natural resources.

Environmental impact:

- Replacement of less environmental-friendly technologies with more intelligent systems with environmental friendliness. (Expected in < 5 years).
- Reducing of material waste losses due to improved service lifetime and reduced corrosion activity. (Expected in 5-10 years).
- Safer working conditions (Expected in < 5 years).
- CO_2 emission reduction due to savings in materials for pre-treatments and paints (Expected in < 5 years).

A social impact on improving the quality of life to European citizens is expected as well:

- Contribution to "quality of life" due to amending of current ecological situation and dissemination of green technologies. (Expected in 1-4 years).
- Contribution to the prevention of man-caused environmental disasters, improving safety. (Expected in 5-10 years.
- The novel technologies in perspective can create the new jobs in respective industries increasing employment. Expected in < 5 years.

2. Main dissemination activities

The dissemination strategy of MUST envisaged at reaching a broad range of audiences, including the scientific and industrial communities, the general public and the key decision makers – Figure 1. All the partners have been encouraged to be involved in the dissemination activities. Specifically, the partners were committed to present the project results in conferences, info-days and other dissemination events; to participate in workshops, to prepare scientific papers for conference presentations or journals, to contribute for the web-site contents, to be involved in training and formation of researchers and to highlight the project results.

2.1 Electronic dissemination

The MUST web portal (www.sintef.no/Projectweb/MUST) highlights the project objectives, achievements and relevant events that were organized. In addition to this portal, several partners have created advertisements in the web pages of their institutions, thus creating additional branches for the project dissemination. Targeted to a large array of audiences, with a high visual impact and a clear and concise language, the MUST video, will increase the awareness of the project.

The research partners participating in the project were selected on the basis of their excellence in particular areas, providing complementarities of expertise and skills needed for the successful project realization. The R&D institutions are also excellent in terms of publication of scientific work. Therefore an outstanding number of scientific publications reporting the project achievements was prepared and published in journals of high scientific impact. Figure 2 depicts the final figures concerning this point. The total number of publications was above 100 during the project lifetime and several are expected after the project. Such number of publications is a clear confirmation of the excellent R&D work developed within the project.

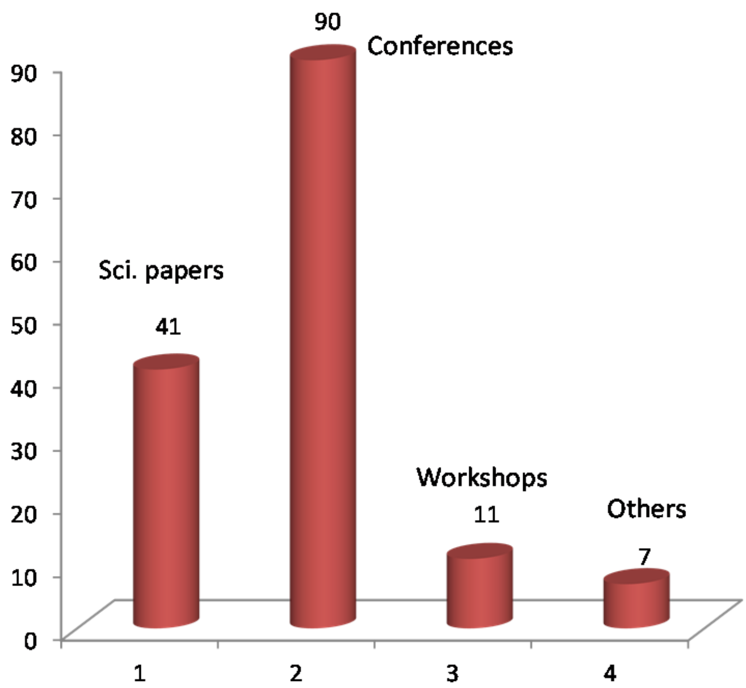

Figure 2 – Scientific achievements of MUST

In addition MUST partners have presented the project in Info days; EUCAR meetings Fumat Conference, EuMAT, etc.

To strength the networking activities MUST organized 4 workshops as listed below.

MUST - Multiprotect workshop focused in the dissemination of MUST objectives and aims and creation of the first layer of networking industrial partners.

Must second Workshop was organized in conjunction with a large coatings conference (COSI)

Life cycle assessment (LCA) & risk analysis in namomaterials-related NMP projects

MUST Final Workshop focused in the MUST achievements and broadening of MUST strategy towards different materials.

2.2 Education and training

Mobility of researchers, at the doctoral and post-doctoral level has been implemented in MUST. This strategy contributed for educating and training high-level researchers, more capable of contributing effectively for the implementation of the R&D and technical activities developed in MUST, supporting the EU research effort.

Six training courses were organized within MUST, both by the R&D and industrial partners:

1. Electrochemical Impedance Spectroscopy, Lisbon, November 6-7 (MUST & MULTIPROTECT) – IST + UAVR
2. Cleaning and Pre-treatment technology, March 9-10 – IST + CHEMETALL
3. Risk analysis – IST + STEINBEIS R-TECH , March 11, 2009
4. LbL of nanocontainers – IST + MPI, October 15-16
5. Adhesion and related characterization techniques, University of Paderborn, September 2010.
6. Adhesives and its testing - SIKA AG Zurich March 16-17 2011.

A total of 19 PhD students (5 PhD theses completed), 7 MSc students (5 Msc theses completed) and 13 post doc students worked for MUST. Thus, MUST actively contributed to the education, formation and training of early stage researchers, thus strengthening the human R%D potential within EU.

2.3 Recommendation and guidelines

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KEY FINDINGS OF EXPLOITATION SURVEYS: EXPLOITATION PLAN AT CONSORTIUM LEVEL

11. **From 37 exploitable results as most desired for exploitation indicated:**

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- Nanocontainers with inhibitors (13 p)
- Nanotraps (13 p)
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12. Time to market

Despite the fact that in some cases additional development and validation work will still have to be done, some of the new technologies may already be implemented within 12-18 months after the termination of the project. Expected time frame for commercial exploitation - Average: 3 years

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14. Intended exploitation (exploitation claims)

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16. Non-commercial Exploitation

- The promising results obtained during MUST will prompt further R&D activities in small, bilateral collaborations with some of MUST industrial partners towards development of systems for commercialization
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4. Concluding remarks

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- Tools for risk assessment
- An exceptional level in terms of scientific publications

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