MUST - Publishable Summary 36 Months

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 second level 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 (third level of protection, see Figure 1). Then a new thin polymer film will be formed, cover the damaged area and repair the layer, preventing crack propagation.

- The highest level of protection 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.

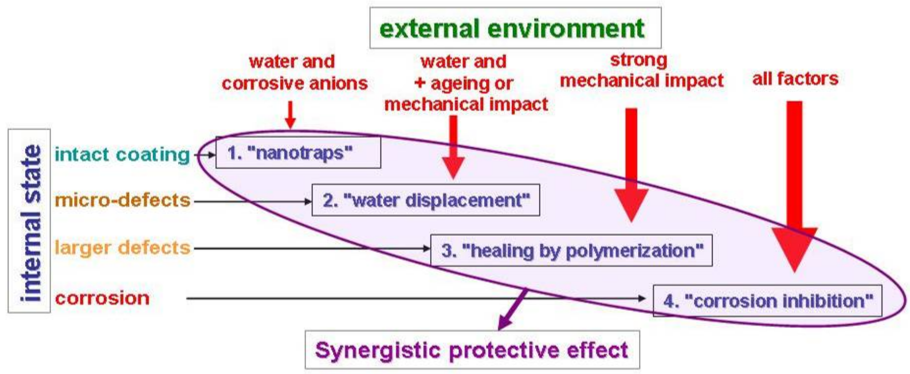


Figure 1 - Illustration of the multi-level protection approach proposed in MUST.

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.

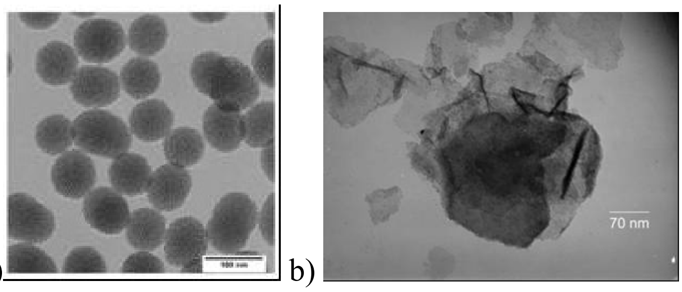
Description of work performed and main results

During 3 years of project execution, the consortium was focused on achievement of the main objectives developing novel self-healing protective coatings and adhesives. The first step in development of the active coatings and adhesives was the creation of new nanocontainers with functional healing agents for different levels of protection. The activity of six partners during the 36 months period was devoted to the development of new nanocontainers using different approaches. Several promising solutions were suggested for all the protection levels.

The highest readiness level was achieved in the case of 4th level nanocontainers loaded with corrosion inhibitors. Several approaches were used to immobilize inhibiting agents inside of different nanocarriers. One of the possibilities was to use mesoporous oxide nanoparticles or hollow inorganic spheres. Nanocontainers composed of silica, titania, ceria, and cerium molybdate were developed. Figure 2 demonstrates one of the examples of such mesoporous oxide nanoparticles developed in frame of MUST project.

Additionally, the surface of the nanoreservoirs could be functionalized with polyelectrolyte shells providing "smart" release of the inhibitor on demand under action of the pH-trigger. Another type of porous nanocontainers was developed using similar shells and natural halloysite clay nanotubes as a carrier.

Ion-exchange based triggering of the inhibitor release was also used to control delivery of inhibiting species on demand. Layered Double Hydroxides (LDH) nanocontainers capable to provide ion-exchange driven release were developed as well. This nanomaterial is composed by positively charged hydroxide layers with compensating anions in the intergallery space. Inhibitor species in anionic form were used as compensations ions. The loosely bonded inhibiting anions from intergallery can be easily exchanged by the chloride ions present in the environment. Thus the nano-pigment is able to work as ion-exchanger storing the inhibiting ions and releasing them on demand only when aggressive chloride anions penetrate to the coating. Additionally LDH were used in first level of protection as well since it is able to play role of a nanotrap of corrosive ions and water, reducing aggressiveness of the corrosive environment.



a) b)

Figure 2 - TEM micrographs of a) mesoporous silica nanoparticles and b) LDH nanocontainers.

The nanocontainers suitable for 2nd and 3rd levels of protection were created using the same encapsulation principles for different functional healing agents such as water displacing agents and monomers, respectively. The main approach here is to employ oil-in-water micro-emulsion interfacial polymerization to provide micro-/nano-capsules of functional agents. Thus the opening mechanisms employed for different types of nanocontainers have been as following: local pH changing, ion-exchange, and mechanic rupture.

The great achievement of the project has been up-scaling of production of the selected nanocontainers from the lab-scale (0.2 L batch) to a pilot-scale (30 L batch) keeping the same performance of the developed materials. In addition, the up-scale to a pre-industrial-scale (200 L batch) is progressing well.

Another indispensable issue in the MUST project is the fundamental investigation of nanocontainers and self-healing processes. Since the topic of self-healing coatings is relatively new, there is lack of existing and well-established experimental protocols for investigation of the self-healing effects. Therefore during the 3 years a lot of effort was invested by MUST consortium in order to develop new experimental techniques or tune existing ones for the needs of the project. A set of complementary experimental methods was created, permitting the investigation of different self-healing mechanisms in a wide range of dimensional scale. The experimental protocols were created to study all four self-healing levels.

Scanning Kelvin Probe Method (SKP) was tuned to investigate the disbonding of the self-healing coatings from metallic surfaces under corrosive conditions. A scanning capillary cell in combination with a stretching device enables us to measure the barrier properties on samples prepared in a well controlled manner. Focused ion beam (FIB) was demonstrated as a promising tool to create well-defined micro-defects in a controllable way. New protocols to study self-healing processes in micro-confined defects employing localised electrochemical techniques were suggested. Spatially resolved electrochemical techniques have the great advantage of giving local information, regarding evolution of the corrosion processes (progress and mitigation) on active defects of the coating. The ability to inhibit corrosion activity in small defects created on the coating surface was deeply investigated by SVET (scanning vibrating electrode technique) and SIET (scanning ion selective electrode technique). One of the innovative approaches is the multilevel corrosion protection that must be provided by combining mixtures on containers loaded with corrosion inhibitors: This protection approach is based on encapsulation of organic and inorganic corrosion inhibitors in different types of nanocontainers acting on demand and suppressing corrosion. Figure 3 presents a coating for the automotive industry that was modified with 2 types of nanocontainers for corrosion protection inhibition. In red, it is possible to see the strong anodic activity on the defect formed on the reference sample. However, very low activity was observed over the defect formed in the coating modified with mixtures of containers loaded with organic corrosion inhibitors. This indicates that nanocontainers answering to different stimulus and presenting different kinetics of release can be used simultaneously to provide corrosion protection on defect formed in the coating. This example illustrates the potential of the combined use of SVET & SIET as an effective assessment of the self healing ability.

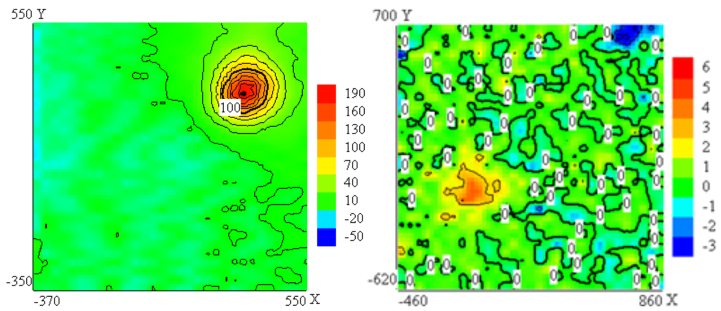


Figure 3 – Corrosion intensity maps obtained on a coating with a defect. Left: reference coating; Right: Coating modified with containers filled with an organic corrosion inhibitor.

The algorithm and computational code for the multilevel protection was developed as well. It considers the presence of water traps and containers with corrosion inhibitor in the multilayer coating, which can be released upon internal trigger (salt concentration, pH) and calculates transport of water and corrosive ions in the coating systems.

The most promising nanocontainers and nanotraps developed in MUST projects are introduced to different functional coatings and adhesives. In several cases, a significant reduction of the corrosion-induced degradation processes could be observed. Figure 4 demonstrates two examples where the introduction of nanocontainers of corrosion inhibitor significantly delays corrosive disbonding of adhesively joined steel surfaces. Introduction of nanotraps for corrosive species into automotive primer also drastically decreases the formation of red rust during the accelerated corrosion tests.

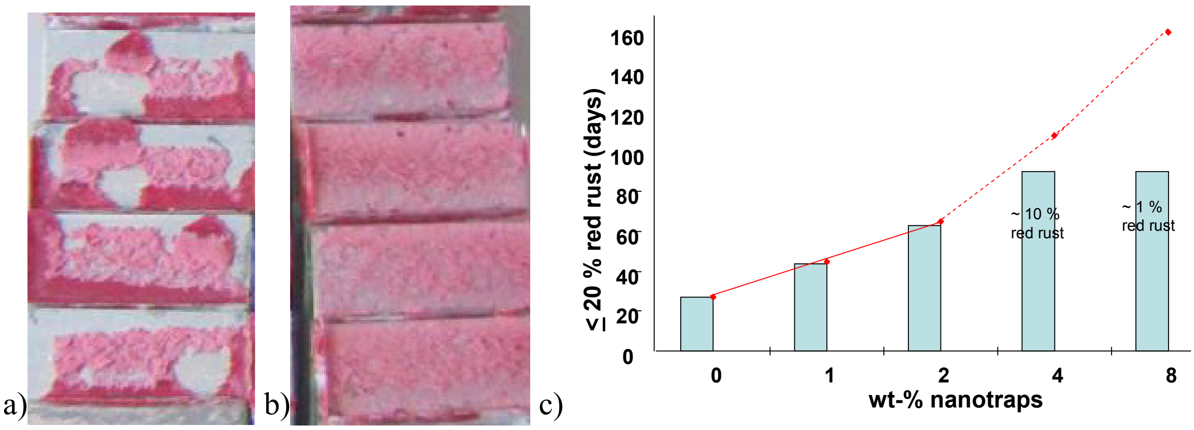


Figure 4 – a) Delamination behaviour of a model adhesive from galvanised steel surface after 20 VDA cycles; b) Delamination behaviour of a model adhesive loaded with nanocontainers at the same conditions; c) red rust appearance on galvanised steel coated with an automotive primer during SST.

The best systems developed in the frame of MUST project are going to be applied on the selected representative demonstrators and tested according to the industrial standards in the next period.

The multi-level protection approach of MUST is based on the integration of functional nanocontainers. Several self-healing protection mechanisms were suggested earlier [4-6] but were never combined together in the same coating system. A gradual protection response of the coating is thereby activated or controlled by specific modes, characteristics and loads of impacts from external environment.

Novel nanotraps able to reversibly absorb corrosive species are in focus of the project. The nanotraps approach suggested will be implemented for the first time. Different inorganic nanostructures such as swelling clays are considered in the MUST project as potential traps.

Oil-in-water microemulsion polymerization is an appropriate technique to encapsulate liquid water-insoluble active agents such as monomers and water displacing compounds. These nanocontainers are of potential interest for 2nd and 3rd level of protection. Moreover, they can be additionally doped with corrosion inhibitors providing complex active protection. Membrane emulsification and ultrasonically controlled emulsion polymerization are used to tune the properties of the nanoreservoirs. Membrane emulsification [7] was applied to prepare nanosized containers from emulsions in the range of 30 nm – 300 nm with low polydispersity (Fig. 3). By a proper choice of materials, multifunctional nanocontainers with suitable compatibility with appropriate coatings may be prepared.

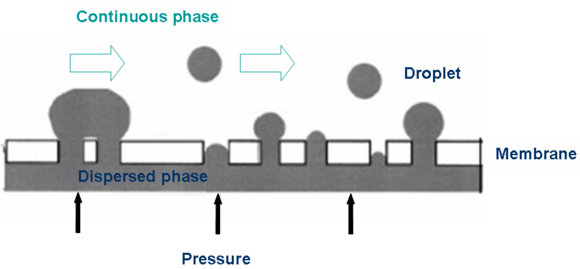


Fig 3 - Principle of preparation of emulsions by membrane emulsification process

Different nano-/meso-porous structures were also used for fabrication of nanocontainers loaded with corrosion inhibitors. After loading with inhibitor(s), the porous nanostructures could be modified with polyelectrolyte layers to achieve release on demand.

Ion-exchange nanopigments were considered as possible "smart" nanocontainers for corrosion inhibitors. They can release inhibiting ions as response to presence of corrosive agents in the environment. Layered Double Hydroxides and nanostructured cationic clays were used for this purpose.

The self-healing processes will be deeper investigated in MUST on the micro-/nano-level crossing the frontiers of existing knowledge. Set of available localised techniques such as SVET/SIET/In-situ AFM together with conventional integral methods will be employed for this.

During the first 36 months the RTD work was mainly focused on the following main objectives:

- Definition of industrial requirements to the nanocontainers and selection of model coating and adhesives to be used in project;
- Lab-scale development of nanocontainers for different levels;
- Detailed study of the developed nanocontainers;
- Formulation of coating systems containing nanocontainers;
- Development of novel experimental methods and protocols to evaluate self-healing properties of the developed coatings and adhesives;
- Study of self-healing of novel coatings;
- Modelling of the self-healing processes as well as processes of nanocontainers formation;
- Tests of model coatings and adhesives doped with nanocontainers according to the requirements from respective industries.

The crucial step of the project is the preparation of nanocontainers to be used in self-healing coatings. The activity of six partners during the reporting period was devoted to development of new nanocontainers using different approaches. The main part of this work was focused on nanoreservoirs containing corrosion inhibitors since this approach is of main industrial interest. Several promising solutions were demonstrated for other protection levels as well.

The first trials on incorporation of nanocontainers to the coating and adhesive formulations for automotive, aerospace and maritime applications have demonstrated that the low amount of available nanoreservoirs doesn't permit reproducible conclusive results at the first stage. After production of the second generation of nanocontainers, new tests series were initiated on modified coating systems. Preliminary tests indicated slightly improved corrosion protection in the case of two tested NCs, which is a promising result. Their effect still must be significantly improved on the next stage. The inhibitor loading capacity in the nano-containers and the total inhibitor amount in the films should be increased. A key issue is related to the compatibility of the nanocontainers with commercial coating and adhesive systems. A strong effort of the consortium during the next project period will be focused on the improvement of the developed systems according to the workplan.

The results obtained in the first stage of MUST are promising and demonstrate a high chance of success of the project. Application of new developed "smart" high-performance materials will sufficiently strengthen the competitiveness of the European transport industries in particular automotive industry.

Expected final results and potential impacts

The coating materials and materials systems that are under development 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. The protection systems developed in MUST will provide 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 this project will directly enhance the economic success and competitiveness of industry. An additional indirect effect on competitiveness will be obtained through improvement of the environmental situation.

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 of the complexity of the protection scheme to be replaced the manufacturing cost for the coating application can be reduced up to 42% utilizing micro- and nanocontainers with reasonable cost.

- 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.

MUST will focus on the development of effective environmental-friendly multi-level active protection systems for materials used in future vehicles.

MUST will increase 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.