MUST - Publishable Summary 52 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 was to develop new active multi-level protective self-healing coatings and adhesives for future vehicle materials. These materials are 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 was 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** combines - 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 have been offered 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 Fig. 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 fig. 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 is utilizing 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.

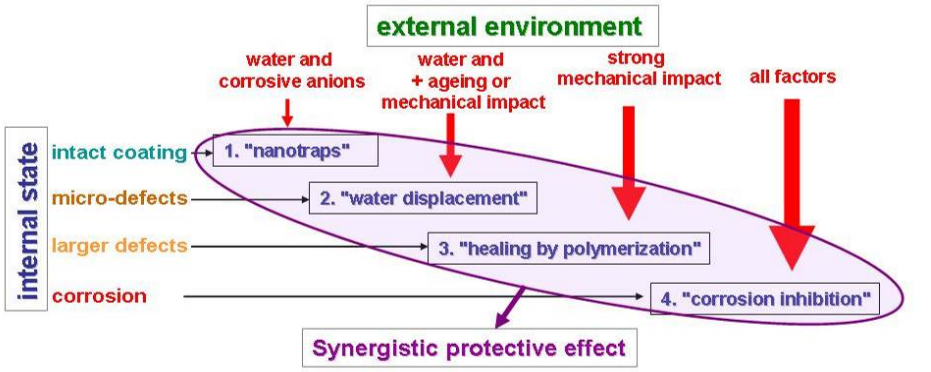

Figure 1 - Illustration of the multi-level protection approach proposed in MUST.

The consortium of MUST was created to meet the main objectives in an efficient way. 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 in setting requirements, 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 academia and research centres and partners from industry (automotive, aerospace and maritime), SMEs and pre-treatment/paint/adhesive suppliers from different European countries.

Work performed and main results achieved

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 4 public workshops, videos and news) and transfer of technology via filing of 5 patents and the creation of 1 spin-off company are among the major impacts of MUST.

Potential impacts and use of the results

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 of 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 will 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 related 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 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 be more than 50% shorter than for a new matrix system.

Another benefit is that the results of the MUST project can be also utilised for multifunctional protection approaches by combination of the MUST solutions with other functions like superhydrophobicity, sensing properties, anti-contamination and anti-erosion.

MUST has been focusing 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. 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.