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Ecoprot, Eco-friendly Corrosion Protecting Coating of Aluminium and Magnesium Alloys, an ECO Innovation Project

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The aim of this project is to industrialise a procedure for producing glass-like, environmentally-friendly and self-healing cerium-based coatings for corrosion protection of aluminium and magnesium alloys. The coatings were developed in a previous Integrated Project, MULTIPROTECT, and the procedure was granted a patent.

The new product is intended for the aeronautic market, where it will be introduced as an environmentally friendly alternative to conventional Cr-based coatings, which provided optimum corrosion protection, but with a major drawback represented by their toxicity. The market will first focus on the French aeronautic sector and will be further extended to address a wider geographical area. The specific objectives to achieve this target are the following:

- Optimization of the coating process for industrial applications (process scale-up)
- Validation of the coated products according to the high standards of the aeronautic industry, in order to ensure replication of the process
- Life cycle assessment of the entire process and the final product, taking into account all production stages, from raw materials to energy and water consumption, end-of-life, etc.
- Business plan to ensure penetration of the final product into the French aeronautic market as a first step and then extend it to other geographical areas.

Description of the proposed solution and summary of the work programme

This project will fill in the gap between the R&D activities that were carried out to develop the coating (MULTIPROTECT) and the commercialization of the final product. The coating systems will be set up to accomplish the specific need of the participating SME (PROMET) by optimizing compositions and synthesis conditions for each substrate and adapting to different primers and finishes, taking into account the current state of the art for each application.

The main idea is the production of the coated systems at PROMET with the collaboration of TECNALIA (the project coordinator) and CSIC (who owns the patent for the coating), then implementing the process for the achievement of the final product for the market. In parallel to this, Quantis will be involved in a Life Cycle Assessment (LCA) of the entire production line, taking into account all phases and integrated

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environmental impacts, including raw materials, energy and water consumption, air pollution, end-of life, etc. TECNALIA with PROMET and iPM^2 will collaborate by assessing a market strategy and a business plan for exploitation of the resulting product, and iPM^2 will lead the dissemination of the results. These tasks involving the penetration in the market in different geographical areas will be undertaken by the other partners as well, taking into account their established international networks.

Major outputs and results (including main result indicators)

The major output of the project will be the market penetration of a sol-gel coating as an environmentally friendly substitution of the chromate processes, which provide an efficient corrosion protection for metal alloys but are characterized by health and environmental toxicity.

The industrial production of the coatings will take place at PROMET, a French SMEs, which will benefit from the market uptake of such a product. The business strategic plan forecast the introduction into the French aeronautic market (main target of PROMET) and further penetration to other geographical areas.
The new product meets environmental standards in terms of procedure and end-of-life treatment, as it does not produce highly toxic waste material as in the case of conventional chromate coatings currently used in the aeronautic industry. In addition, unlike other commercial solutions which are trying to penetrate the market, this coating provides a corrosion performance comparable to that of the toxic chromates, meeting the high standard requirements of the aeronautics industry. The slightly higher price of the product compared to current coatings will be paid off by its greener environmental impact.

Description of the technology, product or process including its innovation aspects.

Chromate conversion coatings represent the benchmark for corrosion protection systems for industrial and aerospace applications because of their high efficiency/cost ratio, including chromate conversion coatings (CCC) and chromic acid anodizing (CAA). They are characterized by self-healing, which is defined as the ability of a material to recover/repair damages automatically without external intervention. However, CrVI based processes must be substituted since they are highly toxic and carcinogenic and they have been banned by all industrial sectors, except aeronautics, since July 2007 (Directive 2000/53/EC). Thus, replacing chromium-based coatings by environmentally-friendly systems triggered the development of protective systems containing alternative corrosion inhibitors. In particular, cerium has shown promise as alternative to chromium-based systems, its inhibiting effect being confirmed by different electrochemical techniques.

Sol–gel technology is an environmentally-compliant method, compatible with organic paints. A key advantage of sol-gel films is the covalent bonding and strong adhesion to the substrate, as well as their barrier effect, limiting the access of the environment to the alloy surface.

The aim of this project is to industrialise a process for producing glass-like, environmentally-friendly and self-healing cerium-based coatings for corrosion protection of aluminium and magnesium alloys for aeronautics application as an alternative to CCC. The cerium-based coatings were firstly developed in the MULTIPROTECT project and the process was patented (Spanish Patent P200930982, PCT/ES2010/070726). The coatings, deposited by dipping and automatic robot spray from sol-gel sols, are densified at reduced sintering temperatures, i.e. below 250ºC. This method produces uniform coatings with amorphous structures and excellent adhesion to the metallic substrates and to a variety of organic primers. Further, the Ce_xO_y glass-like coatings can be used in conjunction with paint systems, primers and/or topcoats, to provide further corrosion resistance. Aluminium and magnesium alloys treated with cerium-based coatings successfully passed diverse accelerated corrosion tests, surpassing the most demanding requirements of the aircraft, automobile and building industries, and providing an alternative to chromium-based coatings.[i]

The Ce_xO_y sol-gel coatings present a glass-like structure, meaning a more open structure with higher enthalpy compared with crystalline CeO_2 films, this being a key innovation of this process. The porous structure and high specific surface area of glass-like coatings aids the lixiviation of cerium ions, with high diffusion rate in amorphous state, triggering their mobility and diffusion to corrosion sites to precipitate, hence passivating and protecting the metal.

For introducing these coatings in the market, the sol-gel process will be optimized for light alloys for aircraft applications and an industrial plant for large scale production of the sol-gel coatings will be adapted to the requirements of the new process at PROMET. The current production capacity at PROMET is a 500 L plant with series of different plating lines; it is possible to envisage a dedicated specific ECOPROT coating line which would work on 8 h/day basis.

Description of any preparatory research, existing prototype or previous tests in real-life

Cerium sol-gel sols with acid and neutral pH, for aluminum and magnesium alloys respectively, were prepared from cerium nitrate mixed with solvents and complexing agents in selected molar ratios to optimise the stability of the sols. The coatings were obtained from up-scaled stable sols up to 10 L in industrial installations (IPA-Plalam-AKABA) and tested in real-life conditions in aeronautic (EADS) and building (Plalam) industrial companies, through standard corrosion tests usually employed in the aeronautic, automotive and other metallurgical industries.

EADS provided sections cut from large demonstrator panels. The main focus of the corrosion tests was the investigation of the stringer areas, where coating thickness was lower due to limited accessibility of the spraying process. The panels were exposed to salt spray test (SST) according to the ASTM B117 standard, up to 1000 h. Only minor corrosion occurred in the scribed region, indicating active protection of the coating system. Filiform corrosion test up to 960 h also showed excellent protection performance. The scratch appeared unchanged, even on stringers or on the welding seam indicating a high resistance of the coatings to the propagation of defects. Alternate immersion-emersion test was also carried out on this system according to DIN EN 3212, revealing protection in the scratched area, and confirming the active protection process.

Glass-like Ce coatings were also deposited on AA3105 demonstrators at IPA and painted at PLALAM by coil coating with polyester based primer and top-coat. The coated and painted panels were tested by adhesion on T-bend and adhesion after embossing. The embossing test showed that the complete system is capable of resisting impact without peeling or cracking. Similar behaviour was observed for T-bend test. The system was bent without flaking or peeling, being evaluated as T1 (very good). Corrosion penetration and adhesion after 1000 h of neutral salt spray (SST) also showed outstanding results satisfying the most demanding industrial requirements.

After finalisation of MULTIPROTECT project, additional lab-scale studies were conducted on AZ91 magnesium alloy with cerium sol-gel sols. Glass-like Ce coatings were deposited by dipping on AZ91 panels at TECNALIA and painted at AKABA with epoxy based primer. The panels were exposed to neutral salt spray and adhesion tests were performed on them. The adhesion test showed that the scratched regions were well adhered and no peeling or material loss was revealed, confirming that Ce glass-like coatings reduce significantly the metal susceptibility to corrosion. A remarkable result of this further research was the main role of the substrates pre-treatment before the coating deposition, this being a critical parameter for the final coatings performance.

Summary of quantified environmental impacts

In the EU-FP6 Project MULTIPROTECT health and environmental hazard factors were investigated in selected materials. Although a full risk assessment was out of the scope, the probability of exposure of humans or the environment to a hazardous amount of inhibiting materials was studied.

For hexavalent chrome the presence in products, like cars and electronics, at the end of the product lifetime is considered an important environmental and safety risk (RoHs and ELV EU directives). MULTIPROTECT basic objective was the development of corrosion protective systems based on active corrosion inhibitors. The inhibiting ions might be released from the coating to act as a repair agent. A high release rate could lead to exposure of humans or the ecosystem to hazardous amounts of inhibitor material. Thus, the release data were used to get a rough estimation of the probability of exposure of humans or the environment to a hazardous amount of the material. Chromate conversion coatings were taken as references.

The lixiviation of inhibitors from Ce_xO_y coatings to demineralised water was tested using the standard procedure ZVO-0101-UV-05, devised to determine the hexavalent chrome content of CCC, that provides a

criterion to establish if a CCC coated material is RoHS or ELV compatible. Test panels of AA2024 and AA3105 with Ce_xO_y coatings were exposed to boiling demineralised water and further analyzed by ICP-AES. Three samples were additionally exposed to artificial sweat, to simulated human body contact, and to rain water solutions to simulated release to the ecosystem. The amount of cerium released from Ce_xO_y coatings in artificial rain water is comparable to that in the boiling demineralised water, whereas in artificial sweat it is below the detection limit of 0.2 µg/cm^2. Taking the acute ecotoxicity of 22 mg/L for water flea exposition, acute toxicity effects from cerium release are estimated very unlikely.
IPA also performed safety tests on Ce_xO_y sol-gel formulations confirming that they are suitable for automatic robot spray process without presenting environmental neither health problems.

Similar or comparable solutions on the market, existing competitors

Nowadays, some non-chromate coatings are available on the market for different applications, but most of them have a much lower performance in terms of corrosion protection than that of chromate treatments. Indeed, none of the new solutions meets the requirements for aeronautics. Although strict regulations on the use of chromates have not been yet established for this sector, there is a worldwide intensive research to replace the CrVI processes and to comply with the high requirements of this sector. **Surface coating industries**, apart from the scientific researchers in R&D Centers and Universities, are trying to develop new competitive protective solutions.

Potential competitors of PROMET in the plating field are mostly SMEs, in France and EU (90% of the France based plating companies are within the 5-50 employees range). Keeping out the more than 250 plating companies members of the French Plating Association only those who could have an interest in such innovative solution, it is possible to select today around 20 potential competitors with comparable plating process range. Some of the coating companies are mainly dedicated to specific customers and/or types of treatments:

- automotive industry
- industrial applications
- jewelery applications
- general plating on small parts
- military application

Although some of the above mentioned coatings have been already applied and tested on aircraft components, they have **not yet penetrated the market** as a complete substitution of Cr-based coatings, because of their **lower corrosion performance** and/or higher price. These coatings provide barrier protection to the substrates, but none of them is characterized by self-healing ability. In addition, some of them are CrIII-based coatings, hence they present environmental hazards. Although CrIII is potentially less toxic than CrVI, it is susceptible to oxidation to the more hostile form, especially during such operation as coatings removing or repairing, recycling of coated components or waste treatment. Thus, it is desirable to look for a solution which is completely Cr-free.

The **glass-like Ce_xO_y coatings** that will be industrialised in this project provide an environmentally friendly solution to the problem, providing **self-healing corrosion behaviour comparable to CCC coatings** apart from other required properties such as good adhesion to the substrate and to organic layers applied on top. Hence this project will be a great opportunity for PROMET to have a highly **competitive position in the market**.

Description of possible technical and economic risks

According to the results obtained during the development of the new coatings and taking into account that the aim of the partners is the substitution of chromate-based solutions, the new product will offer an environmentally friendly alternative to toxic chromates. During the life cycle analysis that will be carried out in the project, the environmental assessment of both materials (new coatings and current Cr-based coatings) will be compared.
The results obtained so far forecast a successful penetration to the market due to the technical performance and positive environmental impact. However, certain key points must be considered:

- Although it has been demonstrated that the coating performance in terms of corrosion resistance is comparable to CCC coatings, the final complete system has to pass the very strict standards of aeronautic industry.
- The market of aeronautics manufacturers is characterized by a certain resistance, as they are usually risk averse when it comes to change.
- The specific coating technology requires the control of drying time and temperature, thus a performing equipment is mandatory. This could be a financial/economical drawback in the case of some small SMEs (although other conventional processes also required control of these parameters).

- A cost estimation of the coating is about 12-15% higher than current Cr-based processes. It may be not a significant increase if environmental issues are taking into account. Moreover, the cost of recycling and waste treatment should surely equilibrate the final cost.

These technical issues with some economic consequences will be considered along the project. The major challenge will be keeping up with the competitive price and performance of the Cr-based coatings, which are still used in aeronautics. However, they are already banned for all the metallurgical sector and the increasingly higher environmental requirements are opening the way to promising alternatives in the aeronautic sector as well.

Identified market barriers to the proposed solution

For the development and implementation of the proposed solution in this project, there are different factors to be considered as potential market barriers:

- **Operational performance** of the solution when evolving from a prototype to an industrial solution: corrosion, adherence to the surface and durability, effect on mechanical properties. Although our previously developed coatings have already proved high standards in these aspects, these will be demonstrated in the industrialized process. Fine-tuning of technical parameters will occur during the project.

- **Costs/competitiveness**. Preliminary cost calculations estimate that the cost of the new Ce based coating on a large scale industrial application could be 12 to 15% more expensive than current Cr-based solutions. Nevertheless, estimates can vary considerably depending on the parts size and geometry. On the other hand, the no toxicity or nocivity of Ce is confirmed against the (economic and societal) costs of recycling and waste treatment for conventional Cr-based processes. Moreover, no alternative solutions are present at the market at the time. Thus it is considered that the non-toxicity and lack of alternatives far outweighs the potential slightly higher cost of the process.

- **Prescription/regulatory issues**. The aeronautics market is characterized by a supply chain (Original equipment manufacturer (OEM), tier 1, 2, 3 suppliers, etc.) where the role, requirements and responsibilities of each player are strictly defined. Thus, the adoption of new technologies in aeronautics is not straightforward, but rather a complex process that has also to take into account a number of standards and regulations. To minimize this challenge some prescriptors (Airbus, EADS, CESA, Iberespacio, see attached Letters of Intent) will be involved in the project, orienting the definition of parts and components where this new coating would be incorporated as well as advising on the evaluation and validations routes and processes. Additionally, there can also be some triggers to speed up the adoption of the proposed coating solution related to new regulatory conditions prohibiting or further limiting the usage of current chromate coatings solutions in the aerospace sector. This has been already the case in the automotive and electronic industries, in which existing regulatory conditions have prohibited the usage of certain materials (chromium, mercury, cadmium, …).

Other potential markets, e.g. aerospace, automotive, will be addressed on a later stage and will benefit by the developments and experience gained in this project, although they might pose market barriers and challenges of thier own, e.g. larger production series (millions vs. thousands), cost considerations (cents vs. euros) and technological alternatives, in the case of the automotive sector.

Market demand and/or results of market analyses

The coating process markets are strongly dependent on the key application sectors: coatings and treatment technologies have historically grown (or receded) based almost entirely on growth patterns in the application sectors.

Recent evolution of European aeronautics turnover demonstrates that this is a growing sector despite the challenging economic conditions Europe is facing. The sector has actually grown in the worst years of the crisis, and it is expected to grow in the coming years above the economy.

The European aeronautical industry accounts for almost half a million employments. According to ASD (Aerospace and Defence Industries Association), France concentrates approximately one third of total European aeronautical industry employment, with 143k positions.

France is additionally a very significant coating market and more specifically the biggest country in Europe for the aeronautics coatings solutions. PROMET (a French company), will bring the coating to the market in a first stage, in selected aeronautical parts and components, mainly associated to the supply chain of big multinational corporations in France. Then, it is envisaged that the technology will be licensed to other coating companies, which can expand its potential application to a wider variety of parts sizes and geometries, and other geographical markets (in Europe, the Americas, Asia,…). As mentioned earlier, introduction of the technology in other sectors (e.g. aerospace, automotive) will be addressed on a later stage, and in the framework of collaboration agreements with companies working in the sector.

Environmental benefits and resource efficiency in a life-cycle approach

In spite of their excellent corrosion protection behaviour, chromates are now declared environmentally hostile, since they are carcinogenic, produce DNA damage, skin allergy, asthmatic reactions, and ulcerations. Consequently, the European Community has forbidden the use of chromate coatings in all industrial sectors, except aeronautics, from July 2007. Thus, replacing chromium-based coatings by environmentally friendly systems has triggered a number of research projects and the development of protective systems containing alternative corrosion inhibitors. In particular, cerium and other rare earth elements have shown promises as alternatives to chromium-based systems, reporting even improved corrosion resistance in some cases.

The novel pure glass-like Cerium-based (Ce_xO_y) coatings investigated and developed by CSIC within MULTIPROTECT and foreseen to be industrialised in ECOPROT project are expected to allow significant savings in terms of life-cycle environmental impacts, compared with conventional chromate-based coatings, for a similar performance in terms of corrosion resistance. The goal of placing in the market these eco-friendly Ce_xO_y glass-like protecting coatings is the total substitution of chromate coatings (CCC) still used in the aircraft industry and the future substitution of the protecting treatments currently applied to light alloys in other industrial sectors, mainly automotive and aerospace companies.

The goal of the first objective is to substitute CCC in the aeronautic industry, by providing a similar corrosion protection and guaranteeing a self-healing behaviour that promotes substrate passivation when corrosion begins.

In order to avoid missing any displacement of impacts (e.g. from one life cycle stage to another, from impact category to another, or from one location/environment to another), the full life cycle of coating applications will be covered within the present project, i.e. from the production (including the consumption of resources) and application of the coating to the use stage and end-of-life. The use stage and end-of-life will be based on two case studies in order to provide results as robust as possible. In addition, a full set of environmental impact categories will be considered, including commonly used GHG emissions (also often referred to as “carbon footprint”) and non-renewable primary energy use, but also impacts on human health, impacts on ecosystems, and water use. For each category, the impact assessment methods will be in line with the main guidelines of the ILCD (International Reference Life Cycle Data System) Handbook.

The environmental performance of Cerium-based coatings will be compared to chromate-based coatings but also to selected alternatives (depending on the availability of data) to chromate-based coatings for specific applications.

A rough preliminary comparison of Cr- and Ce-based coatings has been performed beforehand, showing good promises for Ce-based coatings. In particular, the two coating processes were compared, although excluding the use and end-of-life stages of the coated parts.

According to these first rough results, a reduction of impacts is expected for all environmental indicators considered in this preliminary assessment. In particular, a reduction of 13% and 32% is expected in terms of human health and ecosystem quality respectively, due mainly to the elimination of chromium as an input material and consequently as a toxic contaminant in air and water. It is worth noting that the use and end-of-life stages of the coated part (and the coated part itself) are not included in the scope of this analysis. These aspects will be considered during the project after defining a reference application for the coating.

Referenece

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