LATEST ACHIEVEMENTS IN THE FIELD OF MODERN SURFACE TREATMENT

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ABSTRACT

Metallics and composites substrates are largely used in aeronautics and space. Nevertheless, due to their sensitivity toward external environment, they have to be protected. Surface treatments consist to prepare and activate the surface prior to coating and/or adhesive implementation. The compliance to regulatory, technical, environmental and economic requirements entail the development of new "green" functional coating systems with higher performance. On one hand, there is a need for more advanced coatings for conventional applications and, on the other hand, there is a need to answer the requirements of several new Hi-Tech application. Therefore, Rescoll has developed, since several years, different coatings with specific functionalities such as thermochromy, wear and corrosion resistance as well as biocide and adhesion promotion. These coatings systems will be presented

INTRODUCTION

Metals, such as aluminium, magnesium or titanium and their alloys are used in a myriad of applications especially in aeronautics and space. Indeed, they are largely useful because of their physical characteristics such as stiffness and high strength to weight ratios. Nevertheless, they are highly susceptible when exposed to harsh conditions leading to their deterioration up to the break in service which could have a tragic issue for an aircraft. Surface treatments are therefore achieved on metallic substrates to enhance its durability as well as providing additional functionalities such as corrosion resistance, fire-retardancy, wear-resistance, biocide or adherence promotion.

Up to now, classical surface treatment in aeronautics consists to succession of several stages according to the following sequence: i) degreasing; ii) chemical etching; iii) anodization with/without sealing process; iv) primer coating and v) top-coat deposition. Each step is important because of it will play a crucial role. Degreasing step is important to remove organic contaminants at the metal surface. Chemical etching, generally achieved in acidic condition, consists to remove the natural heterogeneous oxide layer at the metal surface while anodization step favours the growth of a new homogeneous porous oxide layer providing corrosion resistance as well as adhesion of superficial coating or adhesive depending on the application of the substrate. Primer coating is generally dedicated to the corrosion protection as well as adhesion promotion of top-coat layer which provide aesthetic of the coating and resistance to external environment like impact resistance or UV radiation. Such process use chemical components such as hexavalent chromium (Cr^{VI}) derivatives. However, due to its high toxicity toward health and environment, the use of Cr^{VI} compounds have been banned by several directives such as REACH, RoHS and so. For these reasons, studies based on alternative to Cr^{VI} have been largely investigated during the last decade. Up to now, no solutions have been found thus remaining surface treatments of metals as a hot topic. The compliance to regulatory, technical, environmental and economic requirements and trends make have to create a revolution in the way to formulate and implement new generation of coatings. Such coatings have to be strongly adherent with high durability and resistance while an easy stripping is also required. Additionally, coatings need to present several specifications such weak thickness and low weight as well as corrosion and wear resistance. Other functionality such as temperature gauge could be added to the

formulation in order to predict the potential deterioration of a substrate. Several examples of new coatings designed by Rescoll will be presented further.

RESULTS

Since several years, Rescoll has developed number of coatings considering the different requirement previously enumerated. Such developments have been performed with industrial partners and in the frame of risk sharing, B to B, RAPID, European and FUI projects.

Thermochromic coating

Organic Matrix Composites (OMC) materials are increasingly used in aeronautic domain due to their lightness. Nevertheless, OMCs are sensitive to high temperature which could lead to their deterioration. For this reason, it is important to know if section has been exposed to high temperature and time exposition.

In order to identify the temperature range of OMCs' exposition, a functional coating has been developed by Rescoll. The project was based on the use of thermochromic fillers presenting the ability to change of colour when exposed to specific temperature. In this way, such modification will indicate that OMCs have been exposed to high temperature and have to be replaced. Rescoll succeeds to design a coating system providing thermochromic functionality for the desired temperature range without neglecting other specifications such as good adherence and fluids resistance.

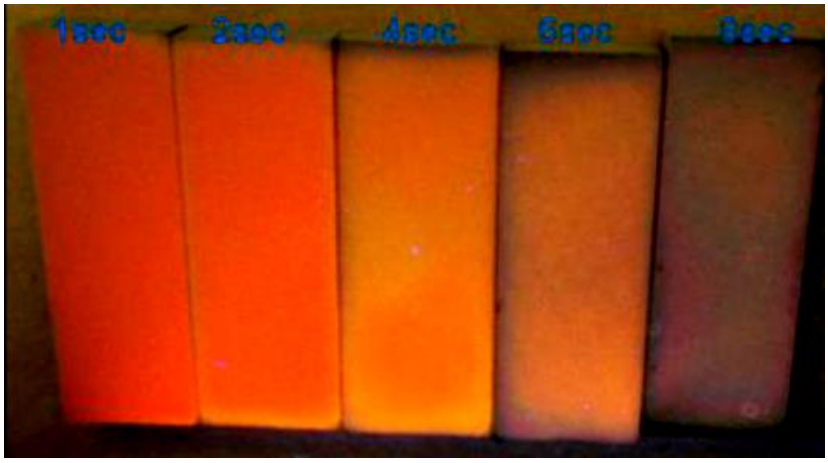

Figure 1: Thermochromic effect for several exposition time at specific temperature.

Wear-resistant coating

Bearings are a critical element in the operation of rotatory elements. The most widely used material in the manufacture of bearings is carbon steel. Indeed, such materials possess excellent mechanical properties, however, bearings using in steel are prone to develop certain types of problems during their lifetime like corrosion, wear, impurities in the substrate or incorrect operating conditions, and are responsible for a decrease in the bearing lifetime.

In this frame, Rescoll has designed a functional coating providing enhancement of fatigue resistance as well as durability of bearings under high loads. Such coating fully respond lubrication specification with a coefficient of friction of 0.22 whitout change in the roughness. Beside this the temperature processing of the coating is relatively moderate close to 100°C.

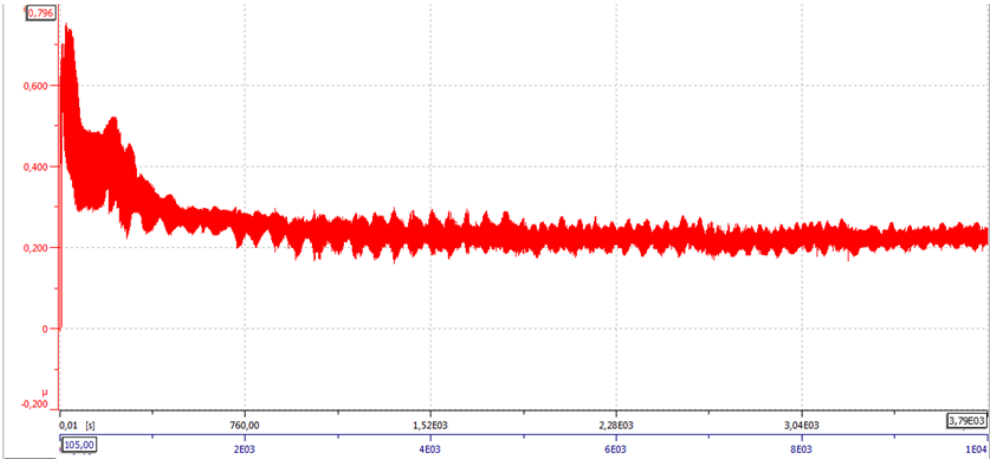

Figure 2: Evolution of coefficient of friction for 10^4 cycles at 2 N.

Adhesion promoter coating

As said previously, composites materials are increasingly used in aeronautics and space due to reduce the weight of the system. In parallel, the joining of aircraft structural elements with adhesive bonding is a key technology to low weight, high fatigue resistance, robustness and an attractive design for cost structures.

Rescoll has developed an adhesion promoter coating for composite material which is also able to degrease the substrate during its implementation. Therefore, such approach will be able to reduce the surface preparation process as well as to functionalize the substrate. It has been shown that coating developed by Rescoll is able to improve adhesion properties by a factor 3 with a cohesive failure in the adhesive when substrate is degreased with the primer.

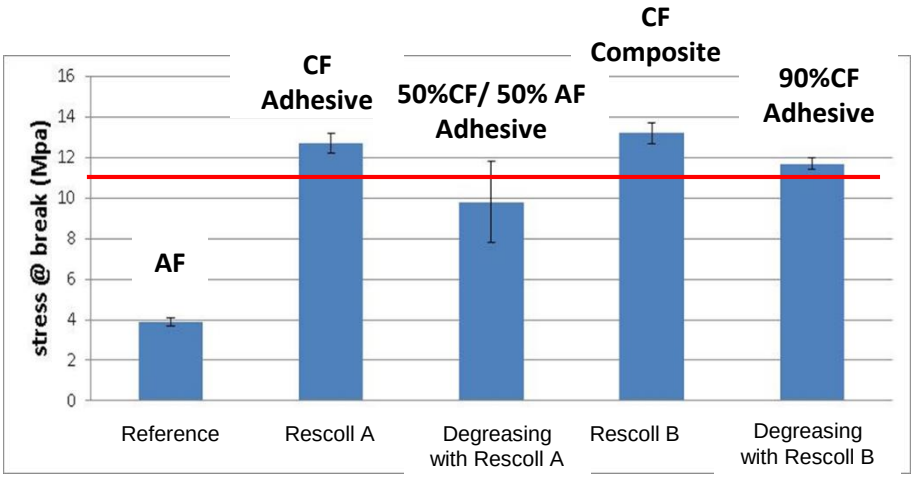

Figure 3: Stress at break and fracture surfaces with different primer developed by Rescoll. CF and AF represent cohesive failure and adhesive failure, respectively.

Adhesion promoter and anticorrosive coating

The “in situ” formed aluminium oxide on aluminium metal surface is usually a sufficient natural corrosion protection. However, the aluminium oxidation occurs in the presence of intermetallic inclusions, which are frequently responsible for corrosion problems of aluminium alloys. Moreover, the adhesion of coatings or adhesive on aluminium is in some cases insufficient. For these reasons, it is necessary to use a coating

system providing corrosion resistance and adhesion promoter. Several solutions are commercially available but only for specific metallic substrates.

On request of his customer, Rescoll has developed a multi-functional coating able to provide corrosion resistance for more than 336 h (Neutral Salt Spray (NSS)) as well as strength resistance more important than 15 MPa. To reach these specifications, Rescoll has designed a coating system by combining different approaches including chemistry route and functional fillers. The appropriate chemistry route promotes strongly the adhesion of adhesive on the metallic substrate and corrosion resistance by establishing covalent bonds with metallic substrate and adhesive and by presenting passive barrier effect due to dense framework, respectively. Moreover, an active anticorrosive effect, also called self-healing effect, is provided by the presence of corrosion inhibitors which could inhibit corrosion phenomenon, on demand, when damage occurs.

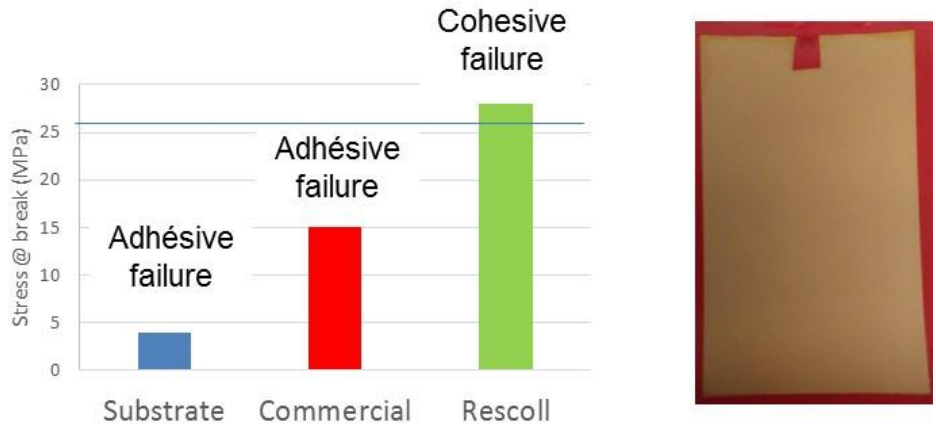

Figure 4: Tensile strength (left) comparison obtained for substrate without and with commercial primer and Rescoll's primer. Rescoll's primer after 336h of NSS (right).

Anticorrosive and biocide coating

From economical point of view, multi-functional "green" coating appears to be a best approach to decrease the number of coatings layers and therefore weight of aircraft. In this vein, several efforts have been made to design coating system providing corrosion resistance and other functionalities such as biocide. Rescoll was involved in multipartenars project, so called SMILE, to design a "green" anticorrosive coating presenting a biocide affect. Such coating was dedicated to the replacement of traditional three chromated layers system by one protective film for gas tank application in aircraft industry. The SMILE technology is based on the development of an hybrid organic – inorganic coating providing passive barrier effect toward aggressive species (i.e. Cl^-, H_2O, O_2…) and structured by an epoxy/amine polyaddition and sol-gel chemistry; respectively. Moreover, corrosion inhibitor and biocide fillers have been added to the formulation in order to provide active protection toward corrosion phenomenon, microbial proliferation and biofilm formation. SMILE system presents excellent anticorrosive with no pitting and corrosion propagation after 3,500 h of exposition to NSS (ISO 9227). Unfortunately, such protective film is prone to filiform corrosion with filaments higher than 4 mm after 1,000 h of filiform corrosion test (FFC) (EN 3665).

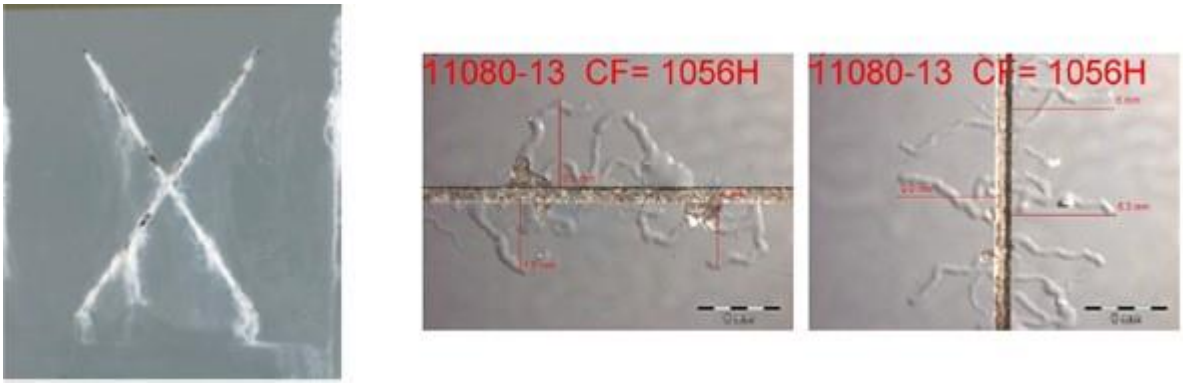

Figure 5: SMILE coating after 3,500 h of NSS (ISO 9227) (left) and 1,056 h of FFC (EN 3665) (right).

Anticorrosive coating

"Green" anticorrosive coating is more than ever a hot topic since the ban of hexavalent chromium (Cr^{VI}) from authorities. Tacking account of the background from SMILE project, Rescoll is actually working on the development of a "green" durable anticorrosive coating in order to replace surface treatments such as anodization and primer coating for structural elements. NSS tests combined with electrochemical impedance spectroscopy (EIS) measurements have permitted to highlight one composition for the hybrid organic-inorganic matrix based on sol-gel chemistry to enhance passive barrier effect. Further, coating formulation have been tuned with different corrosion inhibitor pigments in order to provide self-healing effect. Nevertheless, these techniques (i.e. NSS and EIS) require long time to assess and to rank the pigment behaviour and to optimize the coating formulation pigment content. Hence, Rescoll has recently set up a new accelerated test, namely ACET (Accelerating Cyclic Electrochemical Technique), allowing a rapid screening of the different formulations. ACET results obtained in 24 h correspond to 1,000 h of exposition to NSS and give several information such as barrier properties and corrosion resistance. Finally, the best candidate formulation has been evaluated according to the traditional NNS (ISO 9227) and FFC (EN 3665) tests. Experiments have demonstrated promising corrosion resistance properties with no pitting and no corrosion propagation close to scribed area and only filaments length below 1 mm after 1,000 h of exposure to NSS (ISO 9227) and FFC (ISO 3665) tests, respectively. It is important to note that filaments length obtained for chromated system for FFC experiment is below 2 mm after 1,000 h of exposure highlighting the strong potential of the anticorrosive primer developed by Rescoll.

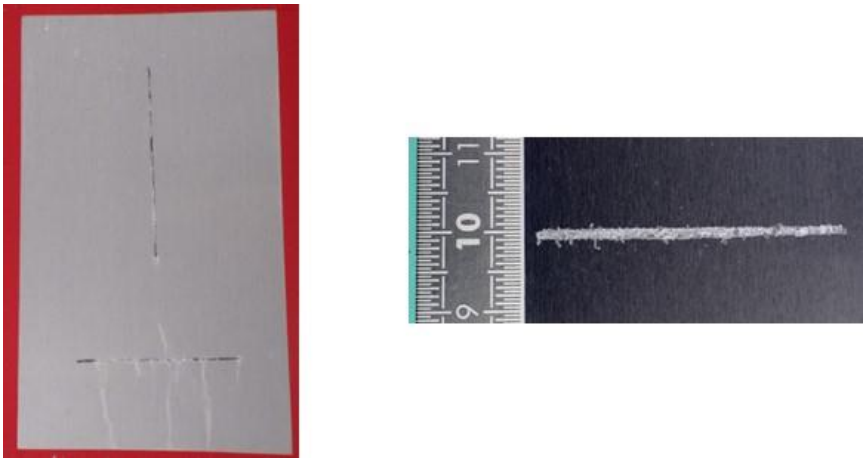

Figure 6: Samples after 1,000 h of exposure to NSS (left) and FFC (right) tests.

CONCLUSION

Surface treatment traditionally used chemical solutions presenting high toxicity, needing drastic controls during the process and, finally, effluents have to be reprocessed. Considering different aspects such as compliance to regulatory as well as environmental and economics requirements, surface treatments have to change to more simple and “green” route. One solution could consist to develop new “green” coating systems providing multi-functional properties such as thermochromy, adherence, corrosion resistance... Due to their strong knowledge in the field of material science and especially in coating formulation, Rescoll, recognised and certified as Technology Resource Centre (CRT) and Contractual Research Company (SRC) in the field of materials, is able to develop functional coating on demand. Such developments occur through partnership with its customer in the frame of risk-sharing, B to B, RAPID, European and FUI projects.