Low carbon coating technologies by hybrid inorganic/organic films

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Among the sustainable coating processes, the hybrid inorganic-organic coating obtained by the sol gel chemistry is a promising technique for the achievement of homogeneous films with improved mechanical properties. Strong reduction of VOC and petroleum dependence may be obtained. The research developed in the protective optical film sector trains many industrial applications firstly the metal corrosion protection through thin film used like a primer or shop primer deposition. Selecting proper wet-reaction parameters and application, the organic/inorganic precursors and additives to promote adhesion firstly, metal substrates can be thin processed. Formulations can be studied starting from the chemical and physical aspects to satisfy many different performance objectives and ambient sustainability...

1. Introduction

The coatings and chemical industries have invested heavily in research to develop sustainable products with reduced environmental impact. When we speak about sustainable process in the coating industrial sector (raw material production, formulation and application), we mean the reduction of all the surface aggressive substances and VOC. There has already been legislative pressure to reduce the use of organic solvents. In Europe, for example, the Solvent Emissions Directive (1999/13/EC) and the Paint Directive (2004/42/EC) have been enacted with the specific aim of lowering emissions of VOCs to the atmosphere. In Italy the N ° 161/2006 law accepted the paint European directive.

Although the development of waterborne coatings and high solids solvent borne coatings has been a success, a number of raw materials that were used in the past, (specifically low MW and N containing additives) are no longer acceptable because of health, safety and environmental concerns.

The global paint and ink market prices 85 bl USD for 27 bl liters[1]; by considering a medium VOC content equal to 35-40% in the solvent borne resin product, we can calculate about 2-2,5 10^6 t of solvent (VOC) in Europe[2].

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[1] www.paint.org/pubs/global_analysis.cfm on 13/10/2009

[2] Based on data W. Paulus - RadTech Europe Conference 2005

All the technologies that do not use any solvents (powder, UV or VOC), are forecast towards an increasing market. Among them, the sol-gel technology strongly reduces the carbon derived substance amount.

Modern concept of sol-gel science agglomerated only during the past few decades. At first, scientific interest was centred on optical characteristics [Schottner, et al.,2003]. From 1980, the technology became attractive in other sectors (Tab.1). The simple, not expensive, sustainable, piece preparation technique associated to the ability to deposit uniform coatings on complex shaped surface is one more advantage together to the mechanical and thermal resistance.

Tab. 1. Sol gel derived materials uses [Uhlmann, et al.,1998].

35 %	Coatings (glass and metal substrates)
30 %	High porosity materials (aerogels, catalyst, mycrofilters, sensors)
15 %	Chemical and biological applications
10 %	Carriers for drugs
10 %	Other (very disperse class)

As for what concerns the coating technology restricted to the range of siloxane materials application, the appealing characteristics are their low surface energy, the thermal stability, the UV stability, the low VOC content (near to 100 g/l while a solvent borne acrylic coating has up to 500-600 g/l), and the alternative to petroleum derived substances.

A very impressionable number of papers have been appeared in the scientific literature during the last 10 years regarding the coating with sol gel derived films [Guglielmi,1997].

Sol gel layers will improve the adhesive bonds of organic binder to the metal without use or generate significant hazardous wastes while eliminating the use of toxic materials like chromates, acid or basic waters from the rinsing of the surface after the acid/base activation. This paper wish to shortly review the recent results obtained with the sol-gel technique, aiming to demonstrate that it is possible to achieve many objectives using inorganic/organic (hybrid) thin film in the surface pre-treatment avoiding dangerous substances.

2. Corrosion and oxidation inhibition

Research activities in the anti corrosion field, are today shifted to find alternatives to Cr-free materials. Sol-gel derived hybrid films offer environmental and health advantage mainly due to aqueous chemistry and inorganic high content. The many types of organic fragments at the same time satisfy many performances. Corrosion inhibition enhancement with thin SiO_2 film obtained by sol gel (tetra-ethoxysilane; TEOS) has been reported in the literature in the ninety years [Kato,1993].

2.1 Adhesion

In approaching the sol gel thin film properties, adhesion is the most relevant parameter to consider as it depends on the chemical and physical differences between the hybrid film and the metal substrate. Thin film adhesion may develop essentially by two different bond types to the surface: weak, second order intermolecular bond, (2-42 kJ/mole) and strong, first order inter-atomic bond (100-1000 kJ/mole). Usually polymer (binder) film adheres to the metal substrate with many weak, second order bonds; however the direct adhesion between metal and organic film require strong surface activation firstly. Using organosilanes on metal, they can condensate over similarly activated, oxidised surfaces, as outlined in fig.1, forming however covalent bonds that have increased resistance to dry thermal shock cycling, and stays intact after performing tape test analysis.

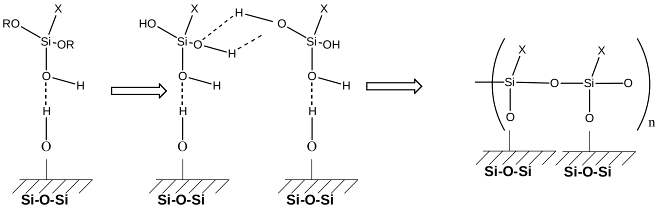

Fig. 1 . Organosilanes condensation over metal oxide. first step: adsorption, second step: hydrolysis with silanols formation, third step: condensation with covalent bonds formation and polymer. (x = organic fragment) [Lamure].

While considering an organic substrate it is possible a different adhesion path that is characterised by an interpenetrated networking that is created on polymer surface and into a short depth by using a suitable solvent mixture.

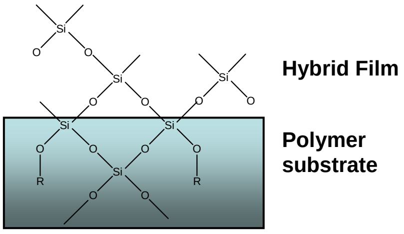

Fig. 2. Interlocking silica network [Chou, et al.,2003]

The schematic image that was experimentally verified (by ESCA) on polyester surface is described on fig. 2 [Chou, et al.,2003]. The polymer surface has to be treated with O_2 plasma or H_2O-H_2SO_4 before the organosilane film deposition to hydroxylate it (fig.1), or with solvents to allow the interpenetrating of the hybrid film (fig.2).

In the first case (metal surface), test in very severe conditions (wet thermal shock cycling) showed an incipient delaminating probably due to hydrolysis of the substrate-O-Si bond and separation of the hybrid coating from polymer surface. The short depth permeate polymer didn't show any instability in the same wet conditions. Consequently in presence of metal surface some types, an induced porous surface may be necessary.

Recently we coated anodised magnesium alloy AM60B using a sol gel technique to inhibit the corrosion by an hybrid double polymerised layer [Bestetti, et al.,2009]. Magnesium alloys has high corrosion susceptibility that limits its utilisation. It has been reported in the literature [Guglielmi,1997] that the polarization resistance of a pure silica coated stainless steel, initially greater than that on bare steel, rapidly decreases owing to the presence of discontinuities in the inorganic film (pores and cracks).

Organic-inorganic, hybrid films may present a significant suppression of the number of the ways to the substrate attack probably related to the extent of the organic cross linking between nanosized inorganic building blocks of the matrix as evidenced in fig.3. Care must be however provided on the choice of organic fragment. We preferred a sol gel formulation composed of TEOS and 3-metacryloxypropyl trimethoxysilane (MEMO) to perform an organic, polymeric, thin film interpenetrated in the polysiloxane chain network.

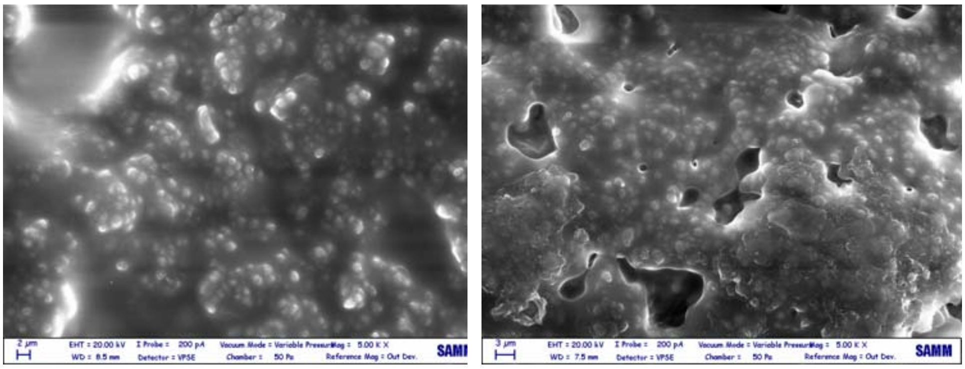

Fig. 3. Sol gel films over Al and Mg-oxide from anodisation, obtained at ambient temperature. The nanosized structure strongly decreases at high temperature [Amoriello,2009].

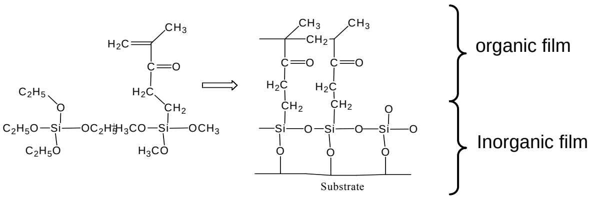

Fig. 4. Schematic picture of a double, organic-inorganic film obtained by a two-step polymerization.

As it is described in the fig. 4, two layers take place: the bottom is covalently linked to the substrate MO and a ceramic type film composes on it, the second is an organic film obtained by radical polymerization initiated by a peroxyacid included in the formulation.

The results agree with a better wear behaviour (flat on cylinder tests) and a decreased surface roughness. The corrosion protection was significantly increased as shown by the electrochemical polarization measurement. By evaluating the results, we accepted that the metal oxide surface is important for the stability and adhesion of the sol gel anticorrosion layer due to the fact that it fasten the hybrid film by allowing the sealing of the pores. We cannot succeed to distinguish the role of covalent bonds surface-O-Si but certainly, as previously observed, it contributes to give a strong adhesion to the substrate and it offer a stabilised layer against the water penetration.

We didn't use colloidal silica as other researchers suggested [Tan, et al.,2005] with the aim to maintain the film more plastic and able to fill the metal anodized pores.

However colloidal silica increases the hardness of the film, changing its morphology and, moreover, we suppose that it may promote the solvent evaporation more uniformly as we observed an homogeneous, not transparent layer from nanosized film obtained during the heat curing step, without any defects as inversely we found in a film without colloidal silica .

Considering the blocking effect alone, a better packing of the small particles has a more efficient anticorrosion inhibition. Like SiO_2 inorganic component of hybrid coating causes a dense covering the metal substrate, so other nano-size ceramic oxides (es.: ZrO_2) inhibits surface attack [Felhosi, et al.,2005]. On the other site, Zn silicate coatings have been used for many years both in solvent or water-borne forms. Their electrochemical inhibition action is crucial to provide corrosion protection. The layer is usually very thin and formulated over the PVC so they possess high porosity which favours the incoming of the water towards the reaction with Zn [Cameron,2004].

However the efforts to reduce VOC, involve a strong interest in reducing the solvent amount which is dependent by the usually used multiple layer paint structure too.

In the hybrid network Zn too may participates to the formation process forming Si-O-Zn-O-Si bonds.

Many patents have been presented in the last years claiming Cr-free composition for anticorrosion achievement. The more recent USP 2009029173 [Scharmm, et al.,2009] claims the use of a two components anticorrosion paint comprising metal pigment, epoxy binder and amine as curing agent. The first example reports the use of γ-glycidiloxypropyltrimethoxysilane (GPTS) which hydrolyses together to bisphenol A to obtain an epoxy, low molecular weight, resin; the resulting short polymer is mixed with Zn flakes and thermally treated. Wetting compatible agent and dispersing agent are used to complete formulation. Deeply examining the patent one can be argued that the philosophy of the anticorrosion designed layer is the same that that before explored by us: one polymer layer and an inorganic layer which may assure adhesion.

3. Compatibility with finishing layers

Sol-gel film at the interface between a metal and a resin may work as primer by furnishing an organometallic layer in the bottom part and an organic silane in the top layer of the compound. Alkoxy zirconium organometallic compound and glicidoxy silane has been reported as an example of this application [Blohoway, et al.,2000]. Generally, the zirconium component bonds covalently with the metal while the glycidoxysilane bonds with the epoxy resin. As previously specified to let stick on the organic top layer, the sol-gel films have to present anchoring sites suited for the chosen polymer binder. One of the advantages of the sol gel coating is the great flexibility of the involved chemistry. Hybrid material can be produced with organic functional group able to bind polyester, polyamine, polyimide, or polyurethane resins. No limitations exist on the possibility to fix organic functional groups in a SiO_2 chain in order to make the pre-coating interacting with the finishing layer.

4. Conclusion

Many research works continuously appear in the scientific literature and patent list on the performances of hybrid films obtained by sol gel route. Its widespread use is, in my opinion, blocked by its wet chemistry not experienced by the applicator. The process is however more sustainable and may overcome many environment issues. The VOC, or the related CO_2 amount reduction, is indeed very relevant (about 6 times).

The use as pre-treatment layer has been demonstrated to be efficient and able to substitute more common anticorrosive layer nowadays adopted. Both Cr based layers, and aggressive chemicals (like phosphate) can be efficiently substituted. The solvent necessary to the corrosive layer deposition can be substituted designing wet based processes. No limits towards new formulations exist due to the high chemical and physical flexibility.

Corrosion inhibition is recognized as one hybrid film advantage strongly depending by the adhesion type that it may develops between hybrid layer and metal surface and, on the other site, between hybrid film and organic layer. Morphology changes that are fundamental for the mechanical properties of film have yet to be deeply investigated and related to specific formulation. Nanosized structure identified in sol gel film may assure mechanical performance.

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