

## Strategies to Optimise Organic Coating Systems

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Organic coatings are generally used for metal protection. The coating process involves several steps, such as chemical pretreatment, priming and application of top coats. Electrochemical Impedance Spectroscopy (EIS) is a valuable tool to tailor each step and/or optimise the protective performances of the complete coating system.

EIS on deformed, T-bent and damaged samples of complete systems can be used as a tool to obtain a selective evaluation of the best chemical pretreatment/primer combinations.

Impedance data analysis and equivalent circuit modeling on undamaged and artificially damaged coatings exposed to aggressive environments can be used to evaluate the influence of formulation parameters, as Pigment Volume Concentration (PVC), on the protective performance and the retention of the coating adhesion, respectively.

EIS data obtained for intact coatings can be analysed to evaluate water permeability coefficients, often influenced by the molecular weight and the chemical nature of the resins constituting the coatings.

Several case histories will be presented to gain further insight on the power of EIS for the optimisation of organic coating systems.

**Key words:** Electrochemical Impedance Spectroscopy, Organic coatings, Industrial applications

### INTRODUCTION

Organic coatings are generally used for metal protection. The coating process involves several steps, which can be summarised as follows:

- metal cleaning
- chemical pre-treatment
- priming
- top coat application

Electrochemical Impedance Spectroscopy (EIS) [1, 2] is a valuable tool for the investigation of reactions and phenomena taking place in different materials [3-8]. It can be also applied to study “at different level” the coating systems. For example, it can be used to study i) the protective performances of the complete coating system, ii) the formulation of a coating layer or iii) the properties of the resin constituting the coating.

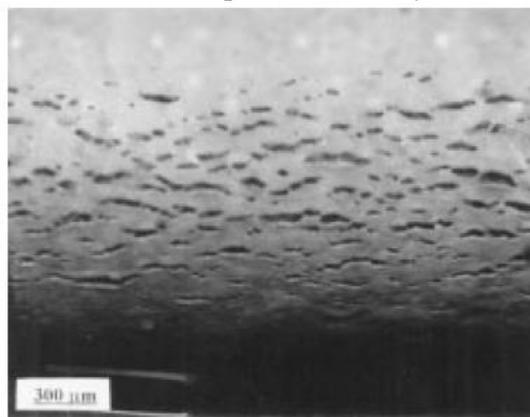
In the following some case histories are presented, to gain further insight on the power of EIS for practical industrial applications in the optimisation of organic coating systems.

### CASE HISTORY 1: OPTIMISATION OF THE PRETREATMENT-PRIMER COMBINATION

The first case history is about the study of the performance of a complete coating system. Coil

coatings are mainly used to coat metal strips which are post-fabricated to desired products later. Coil-coating products are generally tested in quality control laboratories using T-bend deformations. If the metal is pressed together, it gives a 0T bend. 1T, 2T bends, etc., can be obtained with one, two or more thicknesses of the metal around which the bend is made. In this way the flexibility and adhesion performance of the coating as well as its barrier properties are analysed when the precoated metal is produced.

The critical area of the coil-coated products corresponds to the top of the bends, where the presence of induced defects is often unavoidable. Fig. 1 reports the appearance of one bent system, where cracks in the top coat are readily visible.



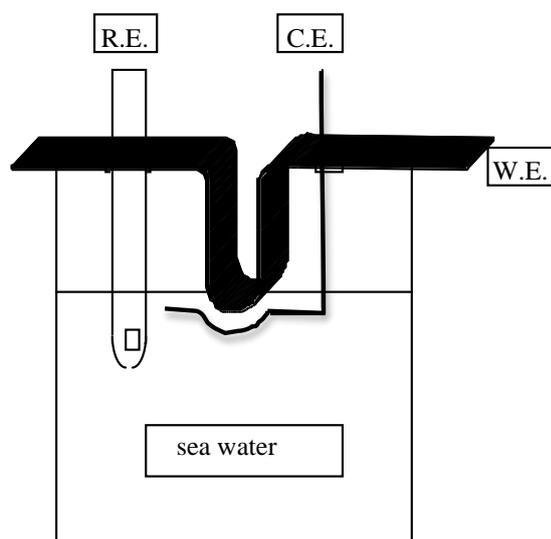
**Fig. 1.** Top of a bend of a coated sample

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The aim of this study was to verify the reliability of innovative pretreatment/primer combinations for a coil coating product.

The materials under test were five experimental pretreatments, named from 1 to 5, in which the reference one, 1, was a nitro-cobalt chemical conversion, and three different primers, named A, B and C, among which the reference one, A, was a modified polyester-urethane resin containing non-toxic inhibitors, which were tested in all the possible combinations.

A three electrode electrochemical cell used for the analysis is given in Fig. 2, where the WE had the top of the bend in contact with the artificial sea water used as electrolyte.



**Fig. 2.** Electrochemical cell for EIS measurements on bent samples

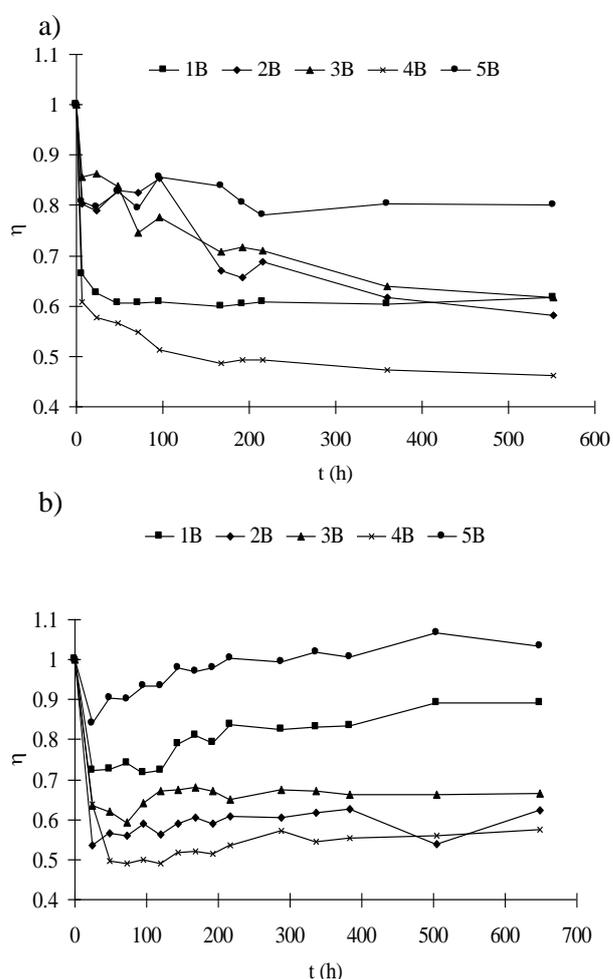
Generally, quantitative analysis of impedance data is carried out over a wide frequency range in order to determine the individual components of an equivalent electrical circuit model that represents the system under test. The high number of pretreatment/primer combinations and the preliminary nature of the analysis led us to consider an alternative way of data interpretation. Since the total impedance of the system at the low frequency can be considered as a rough estimation of the system condition, only the impedance modulus at 0.1 Hz was considered, and recorded as a function of time of exposure to the electrolyte for all the systems. But the different amounts of cracks in the top coat and/or in the primer, and hence the extension of the surface exposed to the aggressive solution at the initial time of the measurement, could greatly influence the initial impedance response, with impedance moduli ranging between  $10^6$  and  $10^8$  ohm  $\text{cm}^2$  at 0,1 Hz.

Then, a relative variation of the impedance modulus was calculated and a degradation factor,  $\eta$ , was defined as:

$$\eta = 1 - \frac{\text{Log}|Z_0|_{0,1\text{Hz}} - \text{Log}|Z_t|_{0,1\text{Hz}}}{\text{Log}|Z_0|_{0,1\text{Hz}}} \quad (1)$$

where  $|Z_0|_{0,1\text{Hz}}$  is the impedance at 0,1 Hz and time 0 and  $|Z_t|_{0,1\text{Hz}}$  is the impedance at 0,1 Hz and time t.  $\eta$  ranges between 1, which is related to the starting condition or no degradation, and 0, which means total degradation of the coating.

Fig. 3 reports the general trend of  $\eta$  as a function of time for some of the specimens with a 4T bend, so low deformed samples, and a 2T bend, as an example.



**Fig. 3.** Degradation factor,  $\eta$ , as a function of time for primer B coupled with all the pretreatments 1, 2, 3, 4 and 5 a) 4T bend; b) 2T bend

It is worth noticing that  $\eta$  constantly decreases for the low deformed samples, indicating a general progressive deterioration of the system; this result can be interpreted as a degradation of the top coat or top coat/primer layers and hence a development of more and larger pores which allow an increasing

water penetration through the first layers of the system. It means that the quite severe bend (4T) did not cause an immediate and complete top coat cracking and this prevents a clear discrimination between the different pretreatment/primer performances. On the contrary, the general defected surface of the 2T bend specimens caused a rapid water up-take through the top coat, allowing a reliable investigation on the inhibitive action of the primer or pretreatment.

The increasing values of  $\eta$  after an initial drop can be readily assumed as indexes of the primer/pretreatment inhibitive action.

Since a clear distinction between the system performance was not possible from these qualitative results, a quantitative attempt was made. Then, the variation of  $\eta$  ( $\Delta\eta$ ) calculated as the difference between the value of  $\eta$  at the time of final measurement and the minimum value of  $\eta$ , generally obtained after an initial time of activation, was estimated. Table. 1 reports the values obtained for the fifteen 2T bend systems.

**Table. 1.**  $\Delta\eta$  values for the 2T bend samples

Primer	Pretreatment				
	1	2	3	4	5
A	0,16	0,07	0,11	0,07	0,11
B	0,17	0,09	0,03	0,08	0,19
C	0,13	0,04	0,07	0,03	0,20

The effectiveness of the system is related to the value of  $\Delta\eta$ : the higher the value, the better the performances. Considering that the combination 1A is the reference one, the performances of the different systems are evident: pretreatments 2, 3 and 4, regardless the primer, have lower inhibitive action than the reference system, while pretreatment 5, coupled with primer A and B, results very promising.

So, from this experience, a fast and reliable strategy to select an effective novel pretreatment/primer combination on a real complete coated system was found.

## CASE HISTORY 2: OPTIMISATION OF THE PVC OF THE TOPCOAT

The second case history is about the study of the formulation of a coating layer.

Paint formulations are complex systems because they are a mixture of a binder, solvents, fillers, pigments and additives. An important parameter that takes into account the balance between most of these components is the Pigment Volume Concentration (PVC), defined as the volume

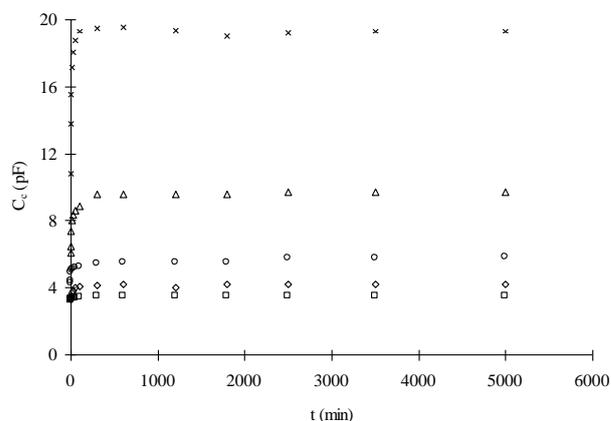
percentage of solid particles in the system after film formation. Depending on this concentration, the properties of the coatings can vary considerably [9]. For example corrosion resistance and gloss decrease with PVC, on the other hand porosity and blistering increase with PVC.

In this work the need of obtaining the best compromise between protective and aesthetic properties of a fluorinated moisture curing coating has been the driving force behind the study of the loading of the system.

The materials were coatings from the same binder, with PVC equal to 0, 5, 7, 10 and 15%. The pigment was a powder of TiO<sub>2</sub>, alumina and amorphous silica.

A series of Q-panels coated with 40  $\mu\text{m}$  of the resins was subjected to impedance analysis to follow the water permeation process. The importance of assessing the water uptake into coatings has been acknowledged because water penetration is an initial step in the degradation process. The initial behaviour of the coatings can be simulated as that of an ideal capacitor, so the impedance results obtained in the frequency range between 1 kHz and 40 kHz were analysed using an R(RC) equivalent circuit and the capacitance was used to evaluate the increase of capacitance of the coating over time. In fact the large difference between the dielectric constant of water (about 80) and that of an organic coating (2-7) evidences if a coated substrate absorbs water. The whole procedure was automated to perform a large number of measurements in the first hours of the experiment.

The water permeabilities of top-coats with different pigment contents are reported in Fig. 4.



**Fig. 4.** Capacitance trends over time for the coatings with PVC: 0,  $\square$ ; 5,  $\diamond$ ; 7,  $\circ$ ; 10,  $\triangle$ ; 15,  $\times$

The starting values of the curves,  $C_0$ , are determined by the composition of the coating and display an increase with the coating pigment

content. This is readily explained considering that the dielectric constant of the fluorinated binder is at least one order of magnitude lower than the dielectric constant of the pigment  $\text{TiO}_2$ .

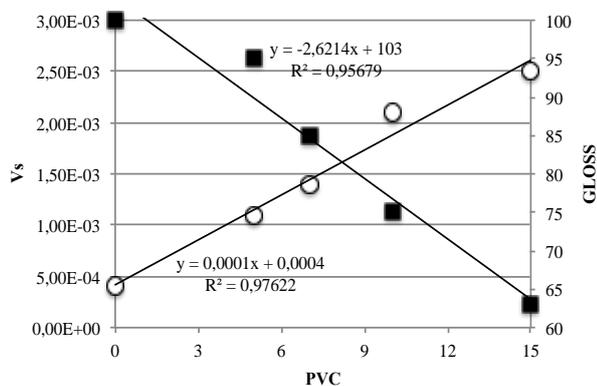
A first stage of water up-take where the coating capacitance,  $C_c$ , increases is followed by a nearly asymptotic trend, which reaches the limiting value corresponding to the saturation of coating voids and porosity by water ( $C_s$ ). Then dielectric constants were converted to water volume fractions through Brasher and Kingsbury equation [10-11], and the volume of water at saturation ( $V_s$ ) vs the pigment content of these coatings was evaluated.

**Table 2.** Volume of water at saturation as a function of the PVC

	PVC				
	0	5	7	10	15
$V_s$	$3 \cdot 10^{-4}$	$1,1 \cdot 10^{-3}$	$1,3 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	$2,5 \cdot 10^{-3}$

The presence of higher pigment contents in the polymer matrix evidently emphasizes the formation of easy pathways for water uptake and/or the presence of voids in the coating structures where excess water can be retained if it is available.

Regarding the aesthetic properties, the gloss, an optical property which indicates how well a surface reflects light in a specular direction, was evaluated too. The maximum gloss is 100, and it decreased with increase of PVC.



**Fig. 5.** Trend of volume of water at saturation and gloss as a function of PVC

Fig. 5 reports the properties of the coating depending on the coating loading. Linear relationships between the parameters and PVC is found.

Also from this experience, a reliable strategy to select the best formulation to obtain optimum compromise between aesthetic and barrier properties specific to our system was found.

### CASE HISTORY 3: CHEMICAL STRUCTURE

The third experience refers to the study of the properties of the coating resulting from slightly different resins.

The polymer network of the binder greatly influence the properties of the coatings [12].

In this work the influence of the chemical nature of the coatings on their technological properties was investigated.

Different polyurethane (PU) coatings were prepared starting from  $-\text{N}=\text{C}=\text{O}$  terminated resins obtained by addition of perfluoropolyether (PFPE) macrodiols of molecular weight 500 or 1000 and cross-linked by exposure to environmental moisture, monocomponent, MC, formulations or by addition of stoichiometric amounts of PFPE macrodiols, bicomponent, BC, formulations. Two series of samples were prepared, characterised by the presence of hexamethylene diisocyanate (HDI) or isophorone diisocyanate (IPDI) polyisocyanurates in the formulation. The samples are generally named with four alphanumeric groups separated by a dash. The first two letters stand for the type of crosslinking: MC and BC. The first number stands for the molecular weight of the PFPE diol in the prepolymer: 5 = 500 or 10 = 1000. The second group of letters stands for the nature of the poly-isocyanurate constituting the coatings: IPDI or HDI. The last number defines the molecular weight of the PFPE used to crosslink the BC coatings.

DSC measurements and stress-strain measurements were carried out on self supported samples, while water permeability tests, through EIS measurements, were carried out on aluminium panels coated with 25–40  $\mu\text{m}$  of the fluorinated polyurethane coatings.

Table 3 reports the technological parameters for the different coatings.

Calorimetric measurements showed that all the coatings are amorphous and most of them are biphasic due to the segregation of a soft PFPE rich phase and a hard, mainly urethane phase. When both well-resolved glass transition temperatures are present, the low Tg value, indicated as Tg F, and the high Tg value, indicated as Tg H, are attributed to the segregated PFPE moiety and to the urethane phase, respectively.

Regarding the mechanical properties of the coatings, they are rather diversified; in general, the use of IPDI leads to harder and brittle materials. In addition, the position of the thermal transition of the rigid phase of the polyurethane markedly affects the mechanical behaviour of the coatings.

The higher the  $T_{gH}$ , higher than room T, the harder and more brittle the coatings. Also the electrochemical impedance measurements gave different spectra depending on the change of the structure of the resin (Fig. 6).

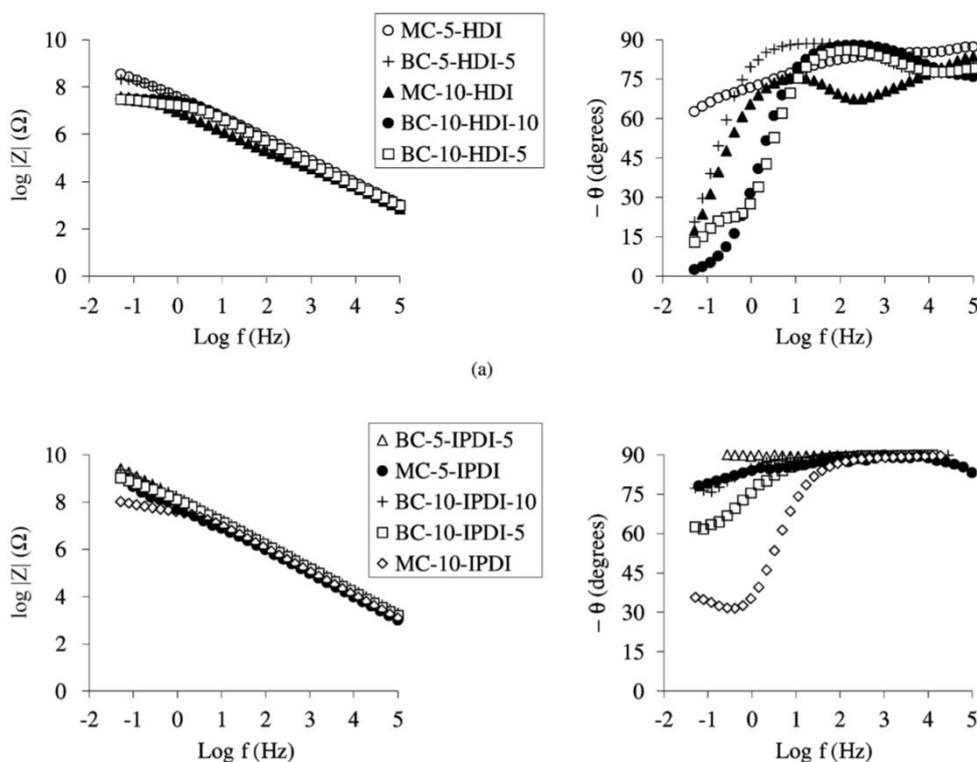
The analysis of the phase shift allows an effective differentiation of the behaviour of the different coatings. From an ideal capacitive behaviour, characteristic of only one coating, BC-5-IPDI-5, the phase shift  $\theta$  decreases at low frequencies and a second time constant, attributed to the electrodic process, appears. On this basis the ranking of the tested materials was determined. Within each series, IPDI or HDI, monophasic structures are characterised by a fine fluorine

dispersion, which guarantees better barrier properties; coatings having Tg higher than ambient temperature are characterised by glassy structures which inhibit water permeation. Comparing the IPDI and HDI series, coatings from IPDI behave better than the corresponding HDI compositions, probably due to the rubbery character of the HDI coatings, whose  $T_{gH}$  values are lower than those of the IPDI coatings and lower than ambient temperature in many cases.

From this work, a reliable strategy to evaluate the wide diversification of structures, morphologies and resulting barrier properties of the final coatings was found.

**Table 3.** Glass transition temperatures and mechanical properties of the PFPE PU coatings

	TgF (°C)	TgH (°C)	Tensile Strength (MPa)	Rupture Strain (%)
BC-10-IPDI-10	-51	52	28,8	25-35
BC-10-IPDI-5	-30	80	31,2	3
BC-5-IPDI-5	10	88	21,3	2
MC-10-IPDI	-67	90	48,6	4
MC-5-IPDI	ND	ND	n.a.	n.a.
BC-10-HDI-10	-61	-22	n.a.	n.a.
BC-10-HDI-5	-60	-7	5,3	80-90
BC-5-HDI-5	-	-1	n.a.	n.a.
MC-10-HDI	-59	41	23,4	40-50
MC-5-HDI	-	50	35,6	4



**Fig. 6.** EIS data for the IPDI and HDI coatings after 4 months of exposure to the electrolyte

## CONCLUSIONS

Electrochemical impedance spectroscopy is a well-established technique for investigating the properties of painted metals. Some simple strategies to apply EIS in the industrial coating optimisation have been shown. Even if the industrial applications of EIS are not very common, in these cases the integration of chemico-physical and electrochemical investigations allowed the enhancement of specific properties of the coatings.

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## Стратегии за оптимизиране на системи за органично покритие

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(Резюме)

Органичните покрития обикновено се използват за защита на метал. Процесът на нанасяне на покритие включва няколко етапа, като предварителна химическа обработка, грундиране и нанасяне на горен слой. Електрохимичната импедансна спектроскопия (ЕИС) е ценен инструмент за проследяване на всяка стъпка и / или за оптимизиране на защитните качества на системата за нанасяне на покрития като цяло.

ЕИС върху деформирани, Т-огънати и повредени образци на завършени системи може да се използва като инструмент за придобиване на селективна оценка на най-добрите химически комбинации за предварително третиране / грундиране.

Анализът на импедансните данни чрез еквивалентни моделни схеми върху неповредени и изкуствено повредени покрития изложени на агресивни среди може да се използва за оценка на влиянието на параметрите на формулиране, като обемната концентрация на пигмент (ПВЦ), съответно, върху защитните качества и съхранение на адхезията на покритието.

Данните получени с помощта на ЕИС, за ненарушени покрития, могат да бъдат анализирани за определяне на коефициентите на водопропускливост, често повлияни от молекулното тегло и химическата природа на смолите, съставляващи покритията.

Разгледани са последователно няколко случая, за да се получи по-задълбочен поглед върху ЕИС като мощен способ за оптимизиране на системите за нанасяне на органични покрития.