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Application of electrochemical techniques to study the effect on the anticorrosive properties of the addition of ytterbium and erbium triflates as catalysts on a powder epoxy network

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Abstract

New low curing temperature epoxy powder coatings cured with *o*-tolylbiguanide and catalyzed by the use of erbium(III) and ytterbium(III) trifluoromethanesulfonates have been formulated. Their curing kinetics and anticorrosive properties have been studied and compared with a system commonly used in industry (*o*-tolylbiguanide/epoxy resin). Three different tests for measuring anticorrosive properties (EIS, AC/DC/AC, and salt fog spray) have been used together with an adherence test, in order to establish the ideal system. Results show that a system using 1 phr of ytterbium triflate presents good anticorrosive properties. The technique AC/DC/AC has shown its ability to evaluate properly and much faster than other techniques the anticorrosive properties of powder coatings with similar results.

Keywords: EIS; AC/DC/AC; Biguanide; Triflate; Powder coating; Salt fog spray

1. Introduction

In the prediction of the anticorrosive properties of an organic coating, the most spread technique is salt fog spray test and its variants. Nevertheless, this kind of techniques is not able to give quantitative information related to the degradation of the organic/metal system. Moreover, they give very subjective information, in some occasions difficult to interpret, they require long times of exposure (1 week to 1 month), and they are expensive to carry out [1]. Thus, in the 1980s, some new evaluation techniques based on electrochemistry were developed to resolve all these problems, being the most used the EIS technique (electrochemical impedance spectroscopy), which has a wide acceptance in the scientific world [2–5]. Despite the good results of this technique, a big problem is still not resolved: the time needed to obtain good results with this technique can be very long depending on the quality of the film (sometimes several months).

Therefore, there is still an explicit interest in rapid assessment methods for practical applications that provide a faster indication of the coating's quality. This technique was initially developed by Hollaender et al. [6] for testing coated metals in food packaging, and successfully adapted by Suay, Rodríguez, and García in the field of liquid and cataphoretic paints [7–11] applied to steel substrates, receiving the name of "AC/DC/AC procedure".

Powder coatings are currently the fastest growing section of industrial paints, because of their favourable environmental attributes (less than 4% of volatile organic contents) and performance advantages [12]. Apart from their clear advantages, powder coatings, show some limitations, like the difficulty of application on thermo-sensible substrates like wood or plastic [13]. Nowadays, the most used powder coating systems are those based on epoxy resins cured with dicyandiamide (DICY) or its derivatives like *o*-tolylbiguanide (TBG) with curing temperatures above 175 °C [14]. For this reason, the formulation of new epoxy powder coatings (using new catalysts and crosslinkers) capable to cross-link at lower temperatures has become one of the main lines of research in industries and related research centres.

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The use of Lewis acid (ytterbium(III) and erbium(III) trifluoromethanesulfonates) as catalysts has given very good results in accelerating the curing reaction between epoxy and *o*-tolylbiguanide (TBG) by the promotion of the polymerization oxirane/NH of the TBG [15]. The question now remains on the influence of the addition of these catalysts on the anticorrosive properties of the system.

In this article it is proposed to study the influence on the anticorrosive properties of the addition of $Yb(TfO)_3$ and $Er(TfO)_3$ on a typical epoxy/*o*-tolylbiguanide system by means of electrochemical techniques and salt fog spray. At the same time, it is studied the validity of the AC/DC/AC procedure on the evaluation of anticorrosive properties of organic/metal systems.

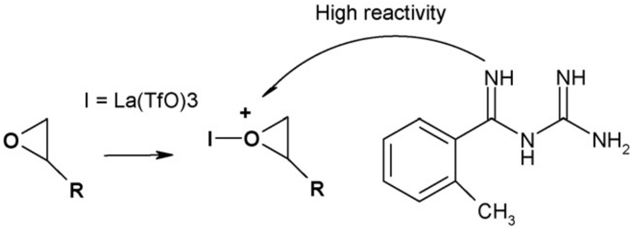
2. Experimental

2.1. Materials

Three powder epoxy clearcoats were formulated using a solid bisphenol-A based epoxy resin of medium molecular weight, 733 g/eq epoxy (from Huntsman), polymerized with 4.8 phr TBG (with an H^+ active equivalent weight of 37 g/eq). One of the samples was catalyzed using 1 phr of Erbium(III) triflate, and another one using 1 phr of Ytterbium(III) triflate, both from Aldrich. The compositions of the samples are detailed in Table 1.

Samples were pre-mixed and hand-shacked until good premixing was afforded. After that, the material was extruded in a single screw extruder (Haake Rheomex 254), with the operating conditions: 80 °C of temperature along the extruder and 60 rpm. The material produced was grinded in an ultra-centrifugal mill ZM 100 and sieved at 100 μm, obtaining then the different powder coatings ready to be applied on steel substrates. In order to know the curing conditions, a complete kinetic study was performed [15].

The different clearcoats were applied on cold-rolled low-carbon steel normalized tests panels (15 cm × 7.5 cm × 0.1 cm). All test panels were degreased with acetone, and paints were deposited by means of a corona electrostatic powder gun (powder coating equipment Easy 1-C), obtaining 10 panels of each sample. The clearcoats were totally cured in an oven for 25 min at 150 °C. Thicknesses determined by an Elcometer were always within the range 60 ± 5 μm.



Scheme 2. Cation oxirane produced by the presence of the triflate.

When using TBG the principal reaction is Scheme 1 [16].

But when adding a triflate as catalyst, the reaction presented in Scheme 1 becomes accelerated because of the creation of the cation oxirane (Scheme 2) which promotes a higher reaction between the epoxy and the amine group of the TBG due to the high nucleophility of the nitrogen (higher than the one of the oxirane ring) [15].

2.2. Testing methods and equipment

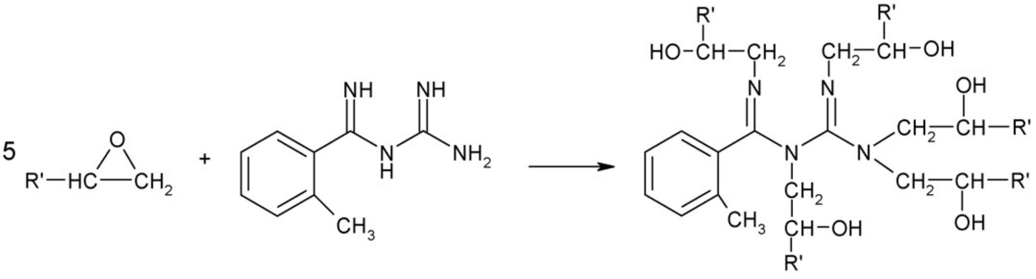
2.2.1. Accelerated cyclic test (salt fog spray)

The accelerated salt fog spray test was performed in accordance with ASTM B 117-85 [17]. In this test a cross is performed along the coating until the bare metal is reached. The samples are then introduced in a salt fog spray chamber were an alkaline fog is created with a 5% (in weight) NaCl water solution. The samples are collected at different periods of time and evaluated until a maximum of 300 h of exposure. After each collection, the samples were dried, and blistering, corrosion and delamination were measured after 24 h of ambient exposure. Delamination was evaluated after applying a tape of 40 mm thick to one arm

Table 1
Composition of the samples studied and glass transition temperature after curing

Sample	Epoxy resin	TBG (phr[a])	Benzoine (phr[a])	Flux agent (phr[a])	$Er(TfO)_3$ (phr[a])	$Yb(TfO)_3$ (phr[a])	T_g (°C)
TBG	100	4.8	0.18	1.27	–	–	95
TBG + Er	100	4.8	0.18	1.27	1	–	101
TBG + Yb	100	4.8	0.18	1.27	–	1	97

[a] phr: parts per hundred resin (w/w).



Scheme 1. Chemical structure of the network using TBG as cross-linking agent.