9TH ARTICLE

Cure Characteristics of Industrial Commercial Paint Using Diffusion Wave Spectroscopy and the Some Properties of Paint Film Determinated by Electrochemical Impedance Spectroscopy

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ABSTRACT

As a contribution to the First International Seminar on Industrial Innovation in Electrochemistry - S3iE - held in Curitiba-Pr, Brazil on 16-17 September 2013 a collaborative work between an institute for applied research and supplier of paints for industrial applications, is presented. In this work the kinetics of the cure paint film based on epoxy high solid with VOC-volatile organic compounds was studied by Multi-Speckle Diffusion Wave Spectroscopy technique. The resistivity of paint film was determined by electrochemical impedance spectroscopy-EIS. VOC paints have industrial applications that require high resistance to corrosion and wear. The control of the kinetics of paints film is of topmost importance to manufacturers and users in diverse industrial applications in different substrates and conditions. In the kinetics studies of film process formation there is three distinct stages. The first stage was attributed to evaporation of the solvent with a small decrease in the fluidity factor. The second stage present a pronounced decrease of the fluidity factor, consequence of increased viscosity of the paint and reorganization of solid paint particles was observed. The last stage is the cohesion of the paint film, i.e., a complete cure. The Diffusion Wave Spectroscopy technique used to study the kinetic of cure of the paint films showed to be very useful to monitor and display the movement of the laser light scattering within the paint films as a function of time. The chemical characterization of the cured film was done by infrared spectroscopy measurement and for EIS measurements a sample of carbon steel was covered with commercial paint.

Keywords: Paint film; Kinetics of cure; Electrochemical Impedance Spectroscopy, Diffusion Wave Spectroscopy.

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INTRODUCTION

Understand the process related with formation of paint films is very important for both paint manufacturers and suppliers of raw material for the manufacture of paints. Due to current laws both from the point of view of care and safety with regard to the handling of chemicals and from the point of view of the final disposition of painted products to the environment, it is primordial an constant innovation to deliver new products that meet not only the laws, but also the new demands of applications. In the case of industrial coatings there is a range of paints, and is an important application for industrial structures operating in harsh environments. To this end, the paint must present some requirements such as high performance in environments that may cause mechanical damage, chemical attack, corrosion and atmospheric immersion conditions. Various characterization techniques have been used to investigate the drying of the coating, and curing the organic coating formation (1-3). In this work, results of the kinetics of curing paint film for commercial industrial applications in harsh environments using the technique of diffuse wave spectroscopy is presented. To investigate the properties of corrosion protection of commercial paint used in this work, measurements of electrochemical impedance spectroscopy on carbon steel painted with an organic coating with thickness of 250 mm were performed.

EXPERIMENTAL

Diffusion Wave Spectroscopy-DWS: for the present study films with wet thickness of 200 µm were prepared with the aid of an extender on glass substrate and placed below the heads laser light of 655 nm with 0.9 W of power. In the experiment, the laser light impinges the paint films, and after the interaction with the constituent particles of the paint it is backscattered. The scattering of light was detected by a CCD camera without lens, displaced by 10 degrees relative to the incident laser light. The kinetics of paint films, manufactured for application for harsh environments, obtained by diffusing wave spectroscopy technique for epoxy paint with high solids and wet thickness of 200µm was recorded with time, where the parameter analyzed is named fluidity factor. The Fluidity Factor is the property used to monitor the structural changes in the curing process of the paint films with DWS technique. In practice register the fluidity factor as a function of time, that is, a direct processing of the backscattered light, which allows accurate quantification of the rate of intensity fluctuations of the images recorded by the camera. The velocity of fluctuation is characterized by correlation time ḉ of images detected by the camera. The correlation time is inversely proportional to the velocity of fluctuation. The correlation time is computed from a set of images acquired by the camera. In summary, the number of images in the set of images and the time elapsed between the recording of two images from the set of images are set respectively for the duration of the acquisition and the acquisition frequency of the CCD camera. The first image from the set of images is taken as the reference image. The displacement of pixels in shades of white and shades of gray between a given image and the reference image recorded is calculated for each whole picture. Thus, the displacement (or distance) inter-image among two images is determined as a difference from pixel to pixel intensity. The correlation time ćof the speckle images corresponds to the time during which the images are still significantly correlated to the first image of the set. When the images of the set are significantly different from the first image correlation ćtime is registered from the set of images and the fluidity factor is determined as the inverse of the correlation time ćand expressed in Hertz (Hz). As a consequence, one plot on the kinetics of film formation results from the processing of a set of speckle images. Because of speckle images this technique has been called Multi-Speckle Diffusion Wave Spectroscopy-MS-DWS (2). Details of experimental setup and fundamentals of the technique can be obtained from some references (1-3). For this work, the paint film is a modified epoxy two-component with high solids (~ 85%) and low VOC.

Electrochemical Impedance Spectroscopy-EIS: the cell was a small piece of carbon steel painted with commercial paint in which a small area was sealed to receive the electrolyte solution of 1.0 M KNO3, a reference electrode of Ag/AgCl and as counter electrode a platinum mesh with high surface geometrical area. EIS measurement was carried out with the help of Autolab potentiostat with impedance FRA32M module.

RESULTS AND DISCUSSION

Diffusion Wave Spectroscopy: in Figure 1 three main stages of the kinetic profile of the cure paint film are observed and indicated in the Figure as stages I, II and III respectively. In the first 52 minutes (stage I), the fluidity factor decreases smoothly, but remains high (> 1 Hz) indicating a rapid movement of the scattering of light inside the paint film. This decrease is associated with the evaporation of the solvent contained in the paint film, that is, the solvent evaporates from the surface of the coating film, the solvent molecules migrate from the liquid phase to the atmosphere due to rapid Brownian movement of the pigment particles in the ink and epoxy with high solid. At the beginning of stage II the fluidity factor decreases sharply indicating a dramatic reduction in the average traffic speed of scattering into the sample paint film. This behavior is characteristic of an increase in viscosity of the system. This stage has been assigned to organization and rearrangement of the particles into the coating film and was defined as the beginning of the packing stage of the particles. The beginning of stage II can be attributed to the exit of the solvent from the interior of the paint film, reaching the complete packing of particles in the final time. This stage in industrial language corresponds to "touch-dry" stage. The fluidity factor reaches a value of around 10-3 Hz at the end of stage II. In stage III, the profile of kinetics the curing process of the coating film decreases smoothly at a rate of about -0.0025 decade of Hz/min until the complete cure of the film, between 14 and 16 hours. The continuous reduction of the fluidity factor in stage III, after complete evaporation of the solvent into the organic coating, shows a steady improvement in the consistency of the paint film. This stage is defined as consolidation of the paint film. The different changes in the slopes of the different stages of the kinetics of the cure are related to changes in the structure of the paint film. In stage I the average slope of -0.0107 was obtained decade of Hz/min and stage II decade of -0.0253 Hz/min.

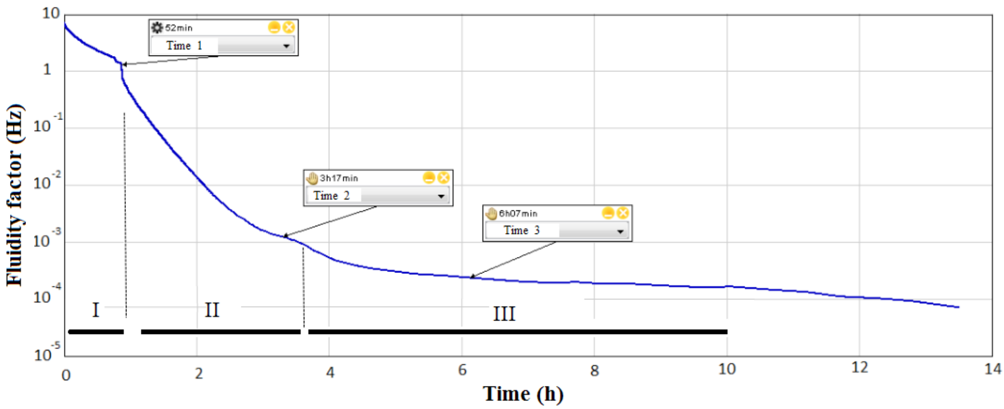

Figure 1. Kinetic profile of the cure of epoxy high solid paint film with a thickness of 200 μm (4).

The final stage of the cure process of the organic film was chemically characterized by infrared spectroscopy and the spectrum is shown in Figure 2. The bands in the spectrum are presented concerning the aromatic rings of bisphenol A which is the basis for the commercial paint used in this work. The bands related to aromatic rings due to axial deformation vibrations of C=C of benzene ring are indicated as 1620 cm-1 and 1500 cm-1. The band bending at 1033 cm-1 refers to the C-O-C asymmetric axial deformation. For the axil deformation the vibration band is 1250 cm-1. The 910 cm-1 band was signed to the axial asymmetric vibration of the binding of the ring of the ethyl ether epoxy. The band at 840 cm-1 is the angular deformation out of the plane of the C-H bond of the benzene ring. The widened at 3500 cm-1 band corresponds to O-H stretching of the hydroxyl groups, revealing the presence of dimers with high molecular weight (5).

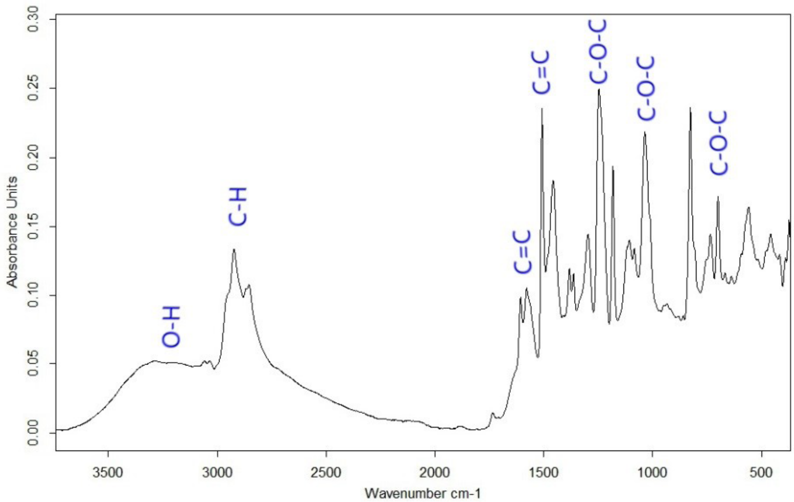

Figure 2. FTIR spectrum of commercial interzone 954 paint film of 200 mm thickness after the cure process.

Electrochemical Impedance Spectroscopy – EIS: the electrochemical impedance spectroscopy is one of the methods used to evaluate protective properties of organic coatings. The EIS also allows monitor the degradation of the paint when exposed to an aggressive environment. In our study we use the EIS to determine the resistivity value of organic coating on carbon steel after cure process, i.e. before expose it in aggressive environment. The environment/organic film/substrate system can be described by equivalent circuit model which can relate the faradaic process of the coating/metal interface and the coating properties, like resistivity and capacitance of the paint film. One well known equivalent circuit model for the environment/organic coating/metal substrate system is presented in Figure 3, where Re is the solution resistance, Rc and Cc are related to the paint film properties and Zf corresponds to the faradaic process of the coating/metal interface. The parameters associated with high frequency are related with the resistance and capacitance of the paint film. For corrosion analysis, the equivalent circuit predicts to the early times of corrosion that sample exhibits behavior of a perfect capacitor and the capacitance of the sample should increase, while resistance tends to decrease due to the permeation of water and aggressive ions when they come into in contact with the metal / coating interface start the corrosion process. In the Figure 4 experimental data of commercial organic coating on carbon steel in Nyquist representation are presented. The data were fitted using the equivalent circuit proposed by Epelboin and are represented in the Figure 4 as dashed line. The obtained value of resistance of the coating film was approximately 1.44x10+9 Ω.cm-2 and de capacitance ~ 0,5 nF. It is evident that resistivity of the fresh cured organic coating is very high; it means that the investigated commercial paint can be considered a very good to be applied as protection against corrosion. In the present work EIS was used only to obtain some properties of the fresh cured organic coating on carbon steel. The degradation of the organic coating can be monitored by EIS as a function of time to get the results for long periods of time in a specific environment.

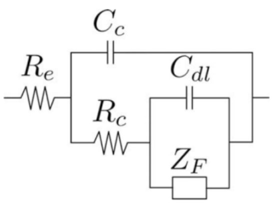

Figure 3. General equivalent circuit proposed by Epelboin (4). R_e is the electrolyte resistance; R_c is the resistance of the solution in the coating; C_c is the capacitance of the coating; C_{dl} is de double layer capacitance; Z_f is the faradaic impedance).

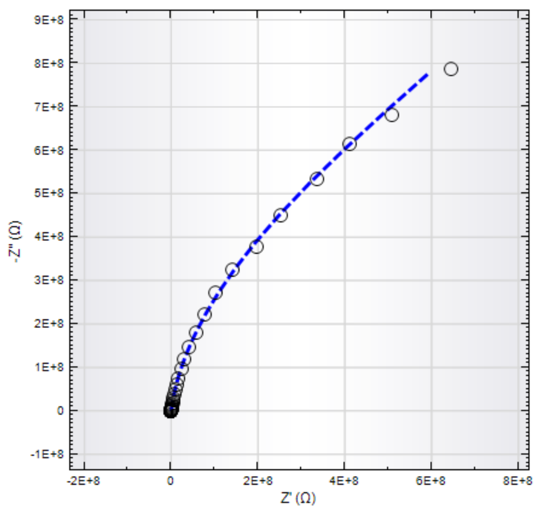

Figure 4. Nyquist representation of impedance values of a carbon steel sample painted with two components with high solids commercial paint. Frequency range of 1.00 MHz to 100 mHz. Amplitude AC signal was 10 mV. Reference Electrode was Ag/AgCl and the counter electrode a platinum mesh. Electrolyte solution was 1.0 M KNO_3. Dashed line is the fitting of experimental data (circle) using the equivalent circuit proposed by Epelboin.

CONCLUSIONS

In this work the technique of diffuse wave spectroscopy was presented to study the kinetics of paint films industrial solvent based. This technique allowed monitor and display in real time the movement of the light backscattered by the particles, interfaces, pigments etc. Three stages of cure kinetics were identified in solvent based paint: I) solvent evaporation; II) rearrangement and organization of the particles and packaging III) consolidation of the paint film. The MS - DWS technique is a non-destructive method to study the process of formation of paint films in conditions similar to those of real or field conditions and provides unique and complementary information for understanding the kinetics of cure (or training) movies paints. EIS is a powerful technique to monitor the degradation of the organic coating, it means, it is useful to help the industries to monitor the corrosion process of metals covered by commercial paint.

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