ATTI ACCADEMIA NAZIONALE DEI LINCEI

CLASSE SCIENZE FISICHE MATEMATICHE NATURALI

RENDICONTI

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# Electrolyte Permeation and Electrical Permittivity of Polymer-Coated Steel as Related to Corrosion of the Substrate

*Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Serie 8*, Vol. **64** (1978), n.3, p. 293–298.

Accademia Nazionale dei Lincei

<http://www.bdim.eu/item?id=RLINA_1978_8_64_3_293_0>

Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Accademia Nazionale dei Lincei, 1978.

# SEZIONE II

## (Fisica, chimica, geologia, paleontologia e mineralogia)

## **Chimica fisica ed elettrochimica.** — *Electrolyte Permeation and Electrical Permittivity of Polymer-Coated Steel as Related to Corrosion of the Substrate.*

Nota di IGNAZIO RENATO BELLOBONO (*) (**), BRUNO MARCANDALLI (*), RENATO MASSARA (***) e LUIGI GUASCHINO (****), presentata (*****) dal Socio G. SARTORI.

RIASSUNTO. — Sono stati studiati due tipi di rivestimenti polimerici su acciaio comune: un poliuretano acrilato ed un acrilico acrilato. Detti rivestimenti (25 μm) sono stati reticolati mediante radiazioni ultraviolette e di essi è stata misurata, a 25 °C in presenza di NaCl 0,52 M, la velocità di corrosione (con metodo standardizzato ASTM D 610), la permittività elettrica in funzione della frequenza, e, con metodo radiochimico, la permeazione, marcando con $^{36}Cl^-$ l'elettrolita. La permeazione all'elettrolita è stata trovata in stretta correlazione con la velocità di corrosione. Il comportamento è discusso alla luce delle più recenti teorie relative al meccanismo di corrosione dei rivestimenti polimerici su metalli.

Two electrical properties may be chiefly considered in investigating the mechanism by which a polymer coating protects a metal substrate against corrosion: *i*) the current response of an isolated film or a coated metal to an applied potential, *ii*) the corrosion potential of the substrate itself. The $d-c$ conductivity of free polymer films have been extensively investigated [1, 2] while the $a-c$ measurements has been treated and discussed [3–6] in terms of equivalent resistances and capacitances. More recently [7, 8] measurements of effective electrical permittivity were performed as a function of frequency and of time of exposure to 0.52 M NaCl. The development of a $-1$ slope on the log loss *vs.* log frequency curve was shown to be the experimental evidence of localized penetration of the dielectric coating by the conducting electrolyte. This behaviour was correlated with the corrosion of the base metal and interpreted by a general model of an equivalent circuit formed by a distribution of series resistors and capacitors in parallel, constituting a heterogeneous assembly of electrolytically conducting paths, each parallel path being a resistor in series with a lossy capacitor. The lossy capacitor is a series connection

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(*****) Nella seduta dell'11 marzo 1978.

of the dielectric polymer and the very lossy metal oxide interface, while the conducting regions represent the electrolyte penetrating the coating randomly over the surface with respect to depth. From this metal / metal oxide / penetrated-coating model, the effective permittivity of the whole system was theoretically formulated [8] and found to be consistent with experimental results. In the present paper this model was applied to investigate experimentally the correlation between the electrical properties and the electrolyte permeation.

## EXPERIMENTAL

### *Coatings preparation.*

Two types of coatings were used in this study: *a*) an acrylated polyurethane [9], and *b*) an acrylated acrylic formulation [9].

A polyester composed of 1,6 hexanediol (3.5 mol), ethylene glycol (1.8 mol) and adipic acid (4.3 mol) was prepared to an acid number of about 1.5.

On the basis of hydroxyl number and molecular weight of this polyester, tolylene diisocyanate (2.2 mol) and 2-hydroxyethyl acrylate (2.4 mol) were mixed with the ester (1 mol) and reacted to give the acrylated urethane.

The acrylated acrylic was prepared by solution polymerization of ethyl acrylate (16.7 wt. %), 2-ethylhexyl acrylate (30.3 wt. %), glycidyl methacrylate (47.3 wt. %) in xylene, followed by addition of acrylic acid (1 mol/mol of glycidyl ester), and heating until the acid number was about 10.

Formulation *a*) was prepared with 65 wt. % of acrylated urethane and 30 wt. % hexanediol diacrylate; formulation *b*) with 50 wt.% of the acrylated acrylic polymer, 30 wt. % hexanediol diacrylate, and 15 wt. % 2-hydroxyethyl acrylate. Both systems were catalyzed with a photoinitiator composed of 2.5 wt. % benzophenone and 2.5 wt. % dimethylaminoethanol.

Common steel specimens 0.025 cm thick, in 10×15 cm pieces, prior to coating with polymer, were manually degreased with Vienna line, thoroughly washed to remove adhering alkaline solution, dipped in 6 M HCl for 20 s, thoroughly washed again with water, and finally with ethanol and ether.

The coatings were applied to the substrate with wire bars to 25 $\mu$m thickness. Curing was effected in air by exposure for 30 s to a 600 watt high pressure mercury arc lamp.

### *Electrical permittivity determinations.*

The experimental cell for capacitance and loss tangent measurements was constructed following the indications given by Kendig and Leidheiser Jr. [8]. The experimental set-up was substantially that used by these Authors, and an air saturated aqueous 0.52 M NaCl solution was employed as permeating electrolyte, at 25 °C. The real and imaginary components of the permittivity

($\varepsilon''$ and $\varepsilon'$ respectively) are related to the equivalent parallel resistance and capacitance by the equations

$$\varepsilon'' = d/A\varepsilon_0\,\omega R$$
$$\varepsilon' = dC/A\varepsilon_0$$

where $\varepsilon_0$ is the absolute permittivity of vacuum, $A$ the apparent coating area, $d$ the coating thickness, $\omega$ the frequency in radians, $R$ the equivalent parallel resistance and $C$ the equivalent parallel capacitance. These two were calculated from bridge balances. The coating and cell dimensions given, the permittivity ($\varepsilon''$ and $\varepsilon'$) could be determined as a function of the frequency between 0.2 and 20 kHz.

### *Permeation measurements.*

Permeation measurements were carried out in a cell similar to that employed for electrical measurements. A perforated steel substrate was used and the hole area was calibrated. The coating was applied uniformly at a 25 μm thickness through the perforated zones. A $^{36}$Cl-labelled 0.25 M NaCl solution was prepared, with a specific activity of 0.35-3.5 mCi/g $Cl^-$, and introduced into the cell over the coating. The substrate cemented to the cell was immersed in water and permeation through the coating, filling the holes of the substrate, determined from the radioactivity increase.

### *Corrosion rate.*

Underfilm corrosion was evaluated by estimating the area covered by corrosion products, following ASTM Standard D 160 [10]: this corrosion rating runs from 10, representing no visible change, to 1, representing a 50 % coverage of the surface by rust.

## RESULTS AND DISCUSSION

Results are reported graphically in Figs. 1–4. Figs 1 and 3 illustrate the log loss *vs.* log frequency behaviour for the acrylated polyurethane and the acrylated acrylic polymer respectively on steel at different times of treatment in 0.52 M NaCl solution at 25 °C.

This behaviour is qualitatively similar to that observed by Kending and Leidheiser Jr. [8]. The appearance of a $-1$ slope at low frequencies in the plot of log $\varepsilon''$ *vs.* log frequency, associated with a path of continuous conductivity through the coating, corresponds to a visibly developing corrosion, while initially or at brief times of exposure to the electrolyte, log $\varepsilon''$ does not change greatly with frequency. In agreement with the predictions of the model used by Kending and Leidheiser Jr. [8], the electrolyte penetrates

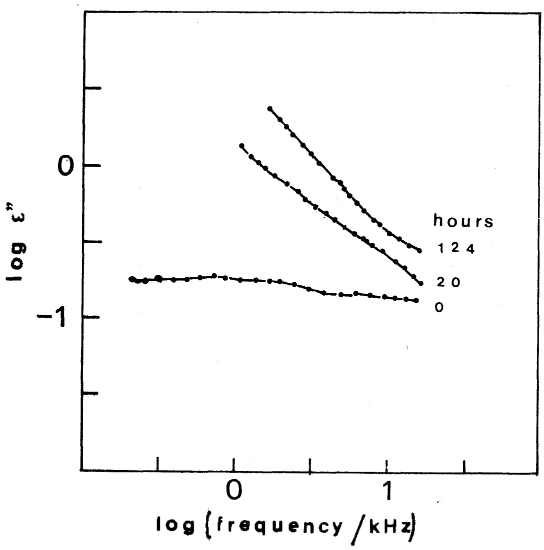

Fig. 1. – Log loss (ε'') *vs.* log frequency for an acrylated polyurethane-coated steel, exposed for 0, 25, and 190 hours to 0.52 M NaCl at 25 °C (coating thickness 25 μm).

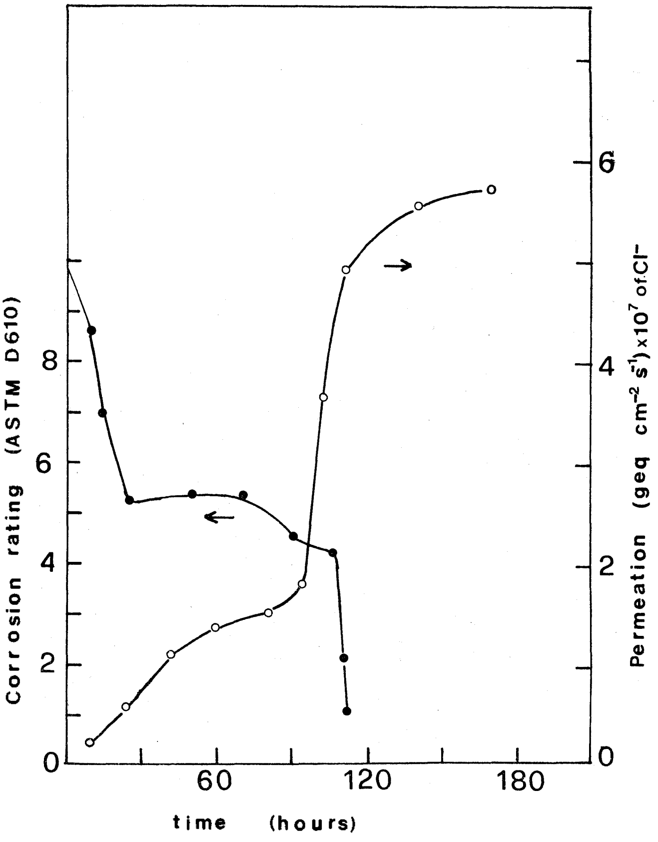

Fig. 2. – ASTM D 610 rating of corrosion (ordinate to the left) and permeation (geq cm$^{-2}$ s$^{-1}$) of Cl$^{-}$ (ordinate to the right) *vs.* time of exposure to 0.25 M NaCl at 25 °C, for an acrylated polyurethane-coated steel (coating thickness 25 μm).

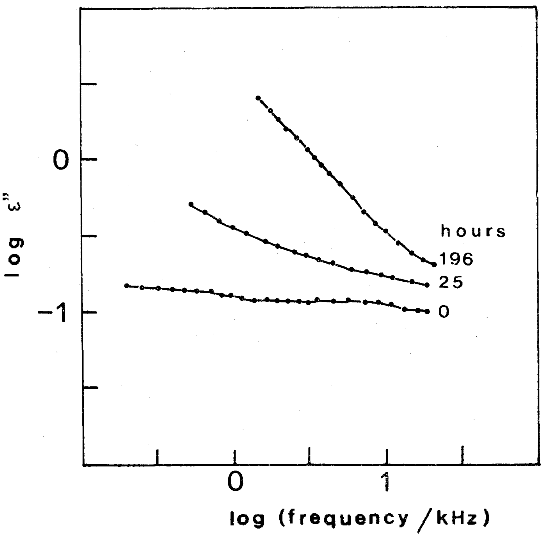

Fig. 3. – Log loss (ε'') *vs.* log frequency for an acrylated acrylic polymer-coated steel, exposed for 0, 20, and 95 hours to 0.52 M NaCl at 25 °C (coating thickness 25 μm).

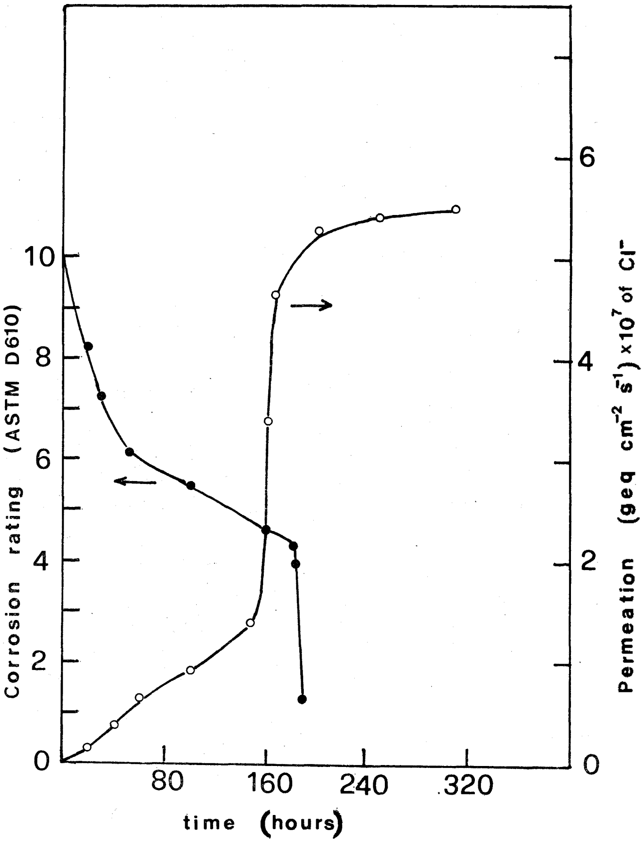

Fig. 4. – ASTM D 610 rating of corrosion (ordinate to the left) and permeation (geq cm$^{-2}$ s$^{-1}$) of Cl$^-$ (ordinate to the right) *vs.* time of exposure to 0.52 M NaCl at 25 °C, for an acrylated acrylic-polymer-coated steel (coating thickness 25 μm).

the coating, setting up conducting paths to random depths over the surface; paths of complete penetration develop with time, allow the electrolyte to meet the metal oxide interface, short circuit the coating and activate corrosion cells.

The validity of this mechanism receives further confirmation by correlating corrosion rates with permeation measurements. Figs. 2 and 4 give results for the two types of coatings investigated. The length of time necessary for the complete failure of the coating as observed by the extension of corrosion products over the entire surface is substantially the same whether measured by visual inspection of corrosion or by the breakthrough curve of permeation. The slight difference between the complete failure time evaluated by these two methods may well be due to a time lag between the activation of corrosion cells over the whole surface and the onset of visible corrosion products everywhere.

The relevance of these results extends from the scientific to the practical point of view. The primary function of a polymer coating on steel is to establish a permanent barrier to the mass transport between the substrate and its immediate environment. Since the current flow associated with corrosion is from the metallic structure to the surroundings, the probability of corrosion occurring is somewhat related to the electrical insulating properties of the protective coating. Cathodic protection current requirements are also governed by the overall dielectric properties of the coating. From this point of view, therefore, the most desirable coating is one that exhibits the highest resistance for the operating life of the facility. Associated with high dielectric strength, however, the permeation properties of the polymer have to be considered, particularly in regard to water vapour and to electrolytes. These latter, which depend on the physical structure of the polymer, but on the physico-chemical caracteristics as well (hydrolysis, ion-exchange) largely determine the overall behaviour and need to be taken into account specifically.

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