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An Historical Perspective on the Corrosion Protection by Paints

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Abstract

Corrosion protection by organic coatings or paints dates back to the beginning of recorded history. Since this time, the technology has advanced through the understanding of the corrosion process and the physics and chemistry of paints. Throughout this history four themes persist: role of electrical properties, role of coating homogeneity, role of adhesion and the role of the paint as a carrier for inhibiting pigments. The aim of this paper is not to provide a comprehensive review of the state of the science but rather to outline the main themes of the research with examples illustrating these themes. To some extent this paper compliments two other reviews in this special issue viz those by Jamali et al and Lyon et al.

Introduction

The use of protective pigmented organic layers, paints, for protecting metals against corrosion dates back to ancient times. Pliny the Elder in 77 AD referred to the rust preventing properties of a mixture of “ceruse” (a white lead carbonate), gypsum and tar (paint) as useful for protecting iron against rust [1].

Corrosion occurs when the corroding metal loses electrons in an anodic reaction leading to metal loss. The electrons move through the metal the metal to sites of cathodic reduction of an oxidant. To balance this charge transfer, ions in the corrosive environment must move between these sites of oxidation and reduction. This model of the electrochemical nature of corrosion has been first attributed to an anonymous paper by L. J. Thénard and R. Mallet appearing in 1819. H. Davy also recognized the electrochemical aspect of corrosion suggesting galvanic protection of copper sheathing of canal boats as early as 1824. Davy’s student, M. Faraday was also an early proponent of the electrochemical aspect of corrosion [2].

Themes

Over the years a number of themes have persisted in the conceptual understanding of the nature of corrosion protection by paints. Early conjectures on the important properties of paint by Newman included suggestions that paint should be perfectly homogeneous and adhere tightly to the bare iron or steel surface while maintaining its elasticity [3]. He went on to suggest that paint prevents the galvanic action by being an insulator of electricity[3].

The authors, with some ninety years of experience of studying anti-corrosive paints between them, believe that the four most important themes which need to be addressed relating to understanding the corrosion protective properties of paints are as follows ::

- (1) Electrical properties
- (2) Coating heterogeneity
- (3) Role of corrosion and corrosion Induced adhesion loss
- (4) Paints as a platform for release of Inhibitors

These themes are covered in the following four sections of this paper.

Electrical Properties

As an introduction to the discussion of the importance of the electrical properties (specifically ionic resistance) of paint in protecting metal from corrosion, we consider the hypothesis of Dr J.E.O Mayne. Mayne observed that paints and organic coatings generally transport sufficient water and oxygen to maintain corrosion of the steel substrate. This leads to the hypothesis that adhesion of the paint inhibits electrochemical reactions though the formation of high resistance pathways between micro and macro anodes and cathodes [4].

For corrosion to take place, electrons must be transferred between anodic and cathodic sites on the metallic surface while ions must be transferred through the solution or corrosive environment. Figure 1 illustrates schematically that a highly resistive pathway placed between anodic and cathodic sites can significantly slow corrosion. With no effective resistance between the respective half cells, a significant corrosion rate will occur. The presence of a resistive layer adds a load line between the two processes effectively slowing the rate (Figure 1). Well adhering non-conducting paints provide such a resistance. In Figure 1, $i_{cor,1}$ represents the corrosion rate with no coating while $i_{cor,2}$ and $i_{cor,3}$ represent the corrosion rates for the material with a resistive paint and a more resistive paint, respectively.

J. Wolstenholme [5] citing the work of Clay [6] suggested that when the polarization resistance of the corrosion process exceeds the coating resistance then the coating has broken down and is not the rate limiting process. A good example of this occurs for paint primers incorporating partially soluble Cr(VI) inhibiting pigments which dramatically increase the polarization resistance of the underlying metal while contributing to a highly conducting coating.

Other electrical properties also relate to paint integrity. For example, a relatively undamaged paint can be considered as a dielectric giving a capacitive electrochemical response. The broad frequency response of the impedance of the film exhibits an inverse frequency and capacitance dependence. Brasher and Kingsbury [7] related the change in capacitance due to the water taken up by the coating through the equation:

$$(1) \quad v = (\log(C_t/C_o))/\log \epsilon ,$$

where v is the volume fraction of water, C_t the coating capacitance after immersion in water, C_o the dry coating capacitance, and ϵ is the relative dielectric constant of water.

Figure 2 shows the water uptake for a coating as determined by a gravimetric method and the more accurate capacitance evaluation [8].

In 1965, Clay [6] used both ac and dc methods to evaluate coating performance. G. Menges and W. Schneider [9] expressed results in terms of ac resistance. Using bridges such as the one shown in Figure 3 (Lehigh University) [11]. Early use of frequency response analyzer methods [10] significantly streamlined the process of gathering broad frequency response of polymer coated steel [10-13].

While most data were expressed in terms of complex impedance Z as a function of frequency, Kendig and Leidheiser [11] expressed their results in terms of a complex dielectric constant, where the complex impedance Z depends on the complex dielectric constant ϵ^* where

$$(1) \quad Z = A/(\omega d \epsilon^*)$$

and

$$(2) \quad \epsilon^* = \epsilon' + j \epsilon''$$

Here A = surface area of the film of thickness d as measured at angular frequency ω and $j^2 = -1$. This enabled the normalization of the data with respect to coating thickness as well as area.

Since the electrical properties of paints and coating have been expressed in terms of complex impedance, broad frequency analysis allowed a description of the coating in

terms of a circuit model, Figure 4, allowing good fit between the calculated and observed data Figure 5.[13]. More recently electrochemical noise has been used with a considerable degree of success [14].

Role of Coating Heterogeneity

It was recognized very early that coating homogeneity plays an important role in the integrity of protective coatings. Localized variations in coating properties provide loci for the initiation and propagation of corrosion of painted metal. Mayne and his students [15] discovered regions differing in electrical resistivity which depended on the ionic concentration of the environment in a direct (D) or an indirect (I) way. These regions have been shown to be localized and correlate with degrees of cross-linking. (Figure 6).[15-18]. The D regions appeared to correlate with loci of corrosion initiation. This was not surprising as other work showed that D areas were small and had orders of magnitude lower resistance than the I areas in Molar chloride solutions. But their resistance was still too high to be explained by the “pores” being filled with the external solution [15]. Kendig and Leidheiser also considered the coating resistivity to be quite localized and proposed the model of distributed “pore” (or D area?) resistances in Figure 7 [11].

Scanning probe methods provided further confirmation of the heterogeneous nature of protective films. These scanning methods included scanning electrochemical impedance [19-20] Scanning Kelvin probe [21], and scanning vibrating electrochemical technique [22]. A differential ac impedance method, Local Electrochemical Impedance Mapping Spectroscopy, or LEIS, combined localized performance and broad band frequency analysis [22-23].

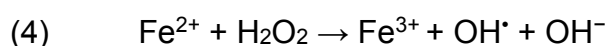
In the early 21st century, Taylor and co-workers used a fluorescent probe ion to demonstrate that both homogeneous and heterogeneous transport of ions occurred through an organic coating. Figure 8 shows a plane view, and Figure 9 the cross sectional views of the distribution of the fluorescent probe. As can be seen, there is both homogeneous diffusion of the ions and certain “hot spots” where a large accumulation of the probe ions penetrate the coating to its base [24-26].

Figure 10 shows the time evolution of the coating “pore” resistance for nominally 8 μm thick polybutadiene coatings on different steel substrates or as a free film exposed to 0.5 M NaCl. The pore resistance was determined from broad frequency analysis. As can be seen, the initial resistances are in all cases similar. However, when the coating is on a corroding substrate the resistance decreases with time

depending on the relative corrodibility of the respective substrate. This suggests that the corrosion process itself influences the transport of ions across the coating as well as having an effect on the degradation of the adhesion of the coating [27]

Role of Corrosion and Adhesion Loss by Corrosion

Funke [28] stated that wet adhesion is essential to corrosion protection while others [29] cast some doubt on this claim. The latter work, however, defines wet adhesion as the adhesion with deionized water transport through the coating. This differs from cathodic disbonding, which is the rate of adhesion loss under conditions of cathodic bias (-1000 mV vs SCE). It is more likely that adhesion under conditions of actual corrosion determines the longevity of coated metal. Localized anodic reactions on both steel and aluminum can drive oxygen reduction adjacent to the attack leading to cathodic degradation of the adhesive bond. Voluminous corrosion products provide a mechanical driver for adhesion loss. Generally cathodic reactions degrade wet adhesion adjacent to regions of high anodic activity as schematically illustrated in Figure 11. Cathodic reactions are singularly detrimental to degradation of adhesion since coatings typically have negative fixed charge such that ionic current is carried by hydrated cations. It is therefore hydrated cation migration to cathodic sites that enhances localized wet adhesion loss. The cathodic disbonding mechanism has been attributed to a number of processes. These include alkaline hydrolysis, oxide reduction, surface energy incompatibility, free radical attack of the polymer as a result of the interaction of the oxygen reduction intermediate, H_2O_2 , with Fe^{2+} via the Fenton reaction:



Where the free radical OH^\bullet attacks the polymer matrix.

There is also evidence applicable to coatings with relatively good adhesion and high ionic resistance that ionic conductivity of the organic coating controls the rate of disbondment under CP (Cathodic Protection) [30]. (For a further discussion on adhesion and cathodic disbondment see [31])

Inhibitors: development of environmentally friendly pigments

Paints provide a platform for holding inhibitors. The inhibiting pigments in paints provide passivation, alkaline buffering, galvanic protection, and *in situ* generated oxygen reduction inhibitors. Inhibitors in the paints can be activated by the corrosive environment.

Recently proposed 'smart coatings' can release inhibitors by electrochemical stimulation of the corrosion reaction. For example, polyaniline can release anion

dopants when cathodically polarized. A coating of polyaniline containing an anion inhibitor placed on a steel surface and then scribed will have an anodic reaction in the scribe whilst the adjacent coating is polarized in the cathodic direction. The cathodic polarization will cause release of the anion inhibitor.

One of the problems with inhibitors is that although effective at preventing corrosion when incorporated into paints they can be toxic. From the earliest days of the development of modern paints, technologists have tried to minimize if not eliminate this problem. In 1908 a paint free from lead was created containing environmentally benign Zn/ZnO pigment. It was shown that this paint could compete well with the corrosion protection provided by lead-based paints [32]. However, it took another 50-60 years to remove lead.

In today's world, several strategies exist for the removal of hazardous solvents from paints. But we still remain on the threshold of completely removing hexavalent chromium from corrosion protective paints. The most often cited pigment replacements for chromate (e.g. Zn and Sr chromate) are phosphates[33], and rare earth-containing inorganics [34-36]. Recent trends include the use of inherently conducting polymers (ICPs)[37] and ICP hybrids [38-39], vanadates [40-42], molybdates and organic/inorganic hybrids[43]. Molybdate-modified Zn phosphate enhances the release of inhibitors that form a nano sized film that inhibits cathodic disbonding [44]. The use of both cationic and anionic exchange materials provide the storage and release of active species including the rare earths, Ca^{2+} , and organic and inorganic inhibiting anions. Yang and van Ooij report use of plasma treated triazol to semi-immobilize soluble inhibitors[45].

A non toxic group of pigments that is generally recognized to act in different way are the sacrificial pigments such as Zn. Metallic Zn has some unique properties that enable it as a sacrificial pigment to ferrous metals. First, it does not corrode too rapidly but remains kinetically semi-passive. Second, the corrosion products of Zn corrosion, Zn^{2+} , mobilizes as a corrosion inhibitor on its own merit. A number of strategies for doing this have been proposed [46]

When it comes to protecting aluminium, zinc, (galvanic series potential of -0.7V vs SHE,) is not sufficiently anodic to aluminum and aluminum alloys. (galvanic series potential 0.5—0.7 SHE) Magnesium (galvanic series potential -1.0 to -1.2V vs SHE) however, has sufficient reducing power to protect aluminum, at least in principle. Bierwagen and co-workers have made progress along the lines of developing an effective Mg-based sacrificial coating. The trick is to slow the self-discharge of the Mg while maintaining its galvanic role. Several un-specified modifications have been shown to improve the performance of Mg-rich coatings[47].

Another group of non-toxic pigments are Inherently conducting polymers (ICPs). These are particularly applicable to normally pseudo noble metals like stainless steel and aluminium. Those currently considered for corrosion protection typically have p-

type conductivity. The stable doped form of these materials bias base metals and alloys to positive potentials above their open circuit potential. Hence their ability, as shown by DeBerry [48], to anodically protect stainless steel in chloride-free environments. Meta-stable organic polymers that electrically couple a reduction potential to the substrate and have an inhibitor for release in a manner similar to that provided by galvanic Zn coatings or Zn-rich paints could provide a new form of galvanization without the presence of heavy metals and with a considerable weight savings. A 2009 report [49] claims to have demonstrated this concept for the case of n-doped poly(2,3-dihexylthieno 3,4-b pyrazine) on AA 2024. In this report, the SVET (scanning vibrating electrode technique) showed negative (cathodic) current at an artificial defect. Other n-doped polymers might also be considered. Whether these materials could be incorporated as a semi-stable component in a coating exposed to an aqueous environment (as the case for metallic Zn) remains to be seen.

As previously reported [50], there is a concept for a chromate generating non-chromate coating which could activate when necessary although the paint as applied would have no hexavalent chromium.

Figure 12 shows a schematic of this concept. The paint contains a benign Cr(III) oxide pigment and an anion exchange pigment containing an oxidizing permanganate anion. The ion exchange protects the permanganate from release unless a corrosive environment containing corrosive anions is present in which case the corrosive anions exchange for the permanganate. The permanganate, in turn, oxidizes a small portion of the Cr(III) oxide to the highly inhibiting hexavalent chromium.

Summary

To summarize this short historical overview of corrosion protection by paints, consistent themes of investigation and discovery point to the fact that paint coatings provide more than just a barrier to corrosive environments. The ionic resistance of the paint coating decouples the anode and the cathode halves of the corrosion reactions. The coating provides a platform for holding corrosion inhibitors. Limits to the corrosion protection by paints result from the nature of the heterogeneities ('pores' or 'virtual pores') in the paint films. There is no doubt that adhesion of paints is important, but specifically adhesion under conditions of corrosion and the presence of wet environments. Future improvements of protective coatings will be in the development of ever more effective inhibitors to replace currently existing hazardous materials.

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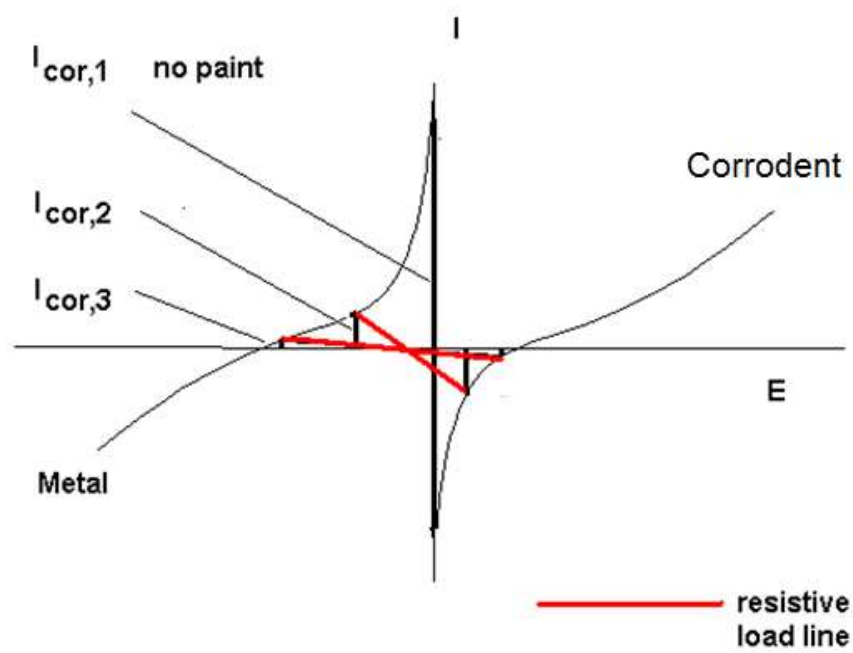


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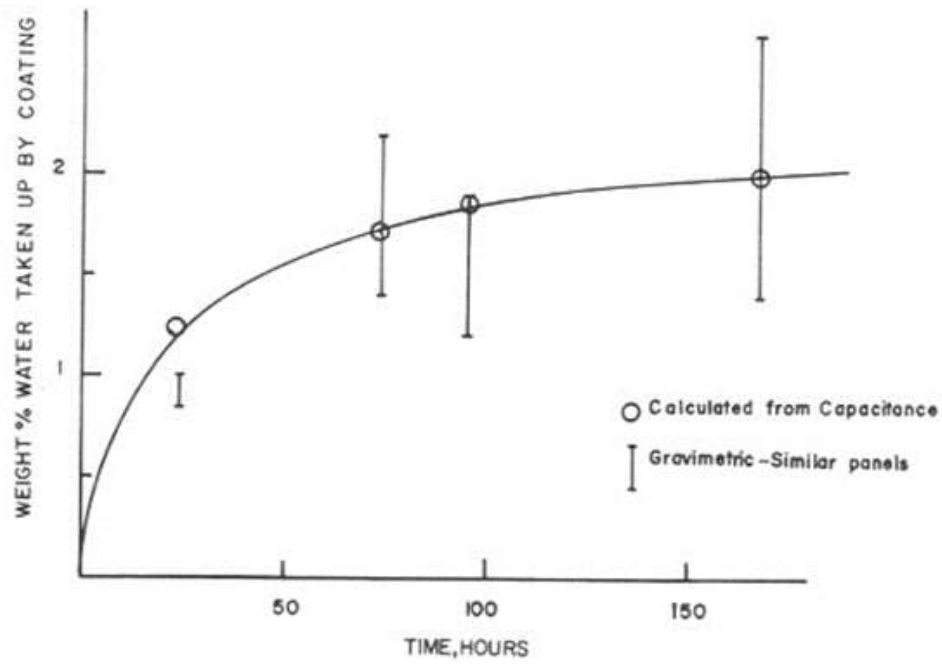


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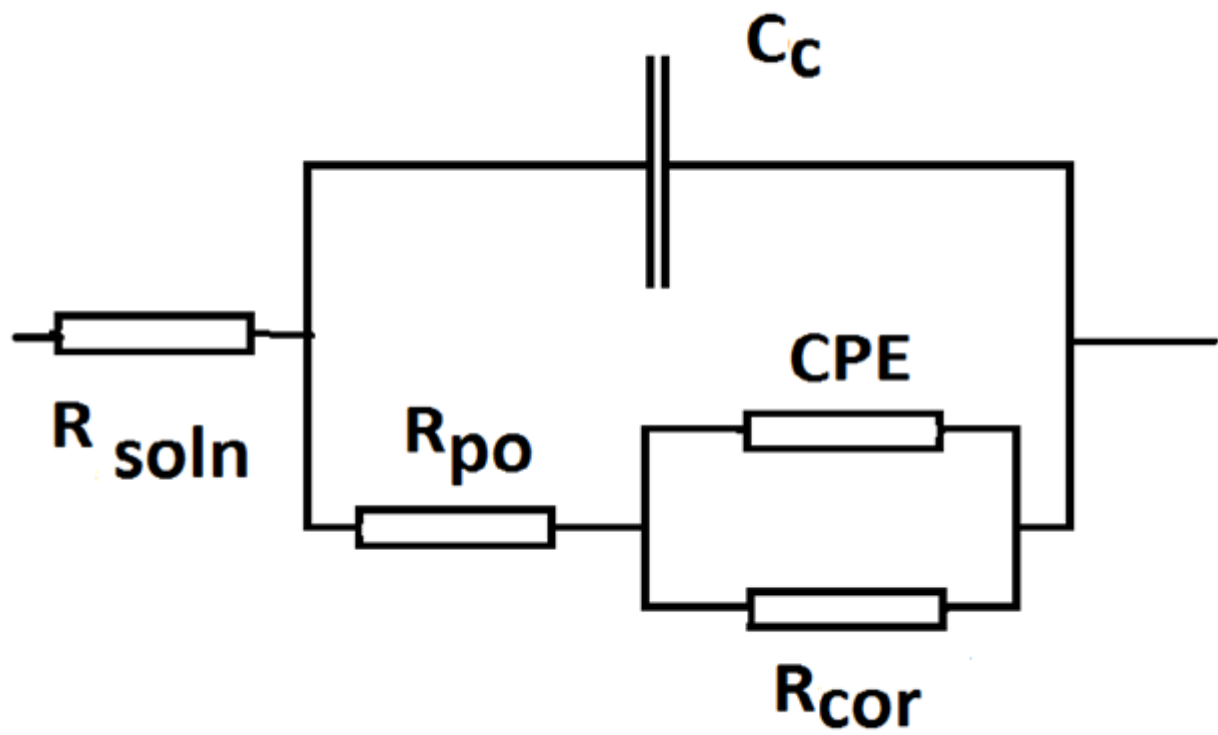


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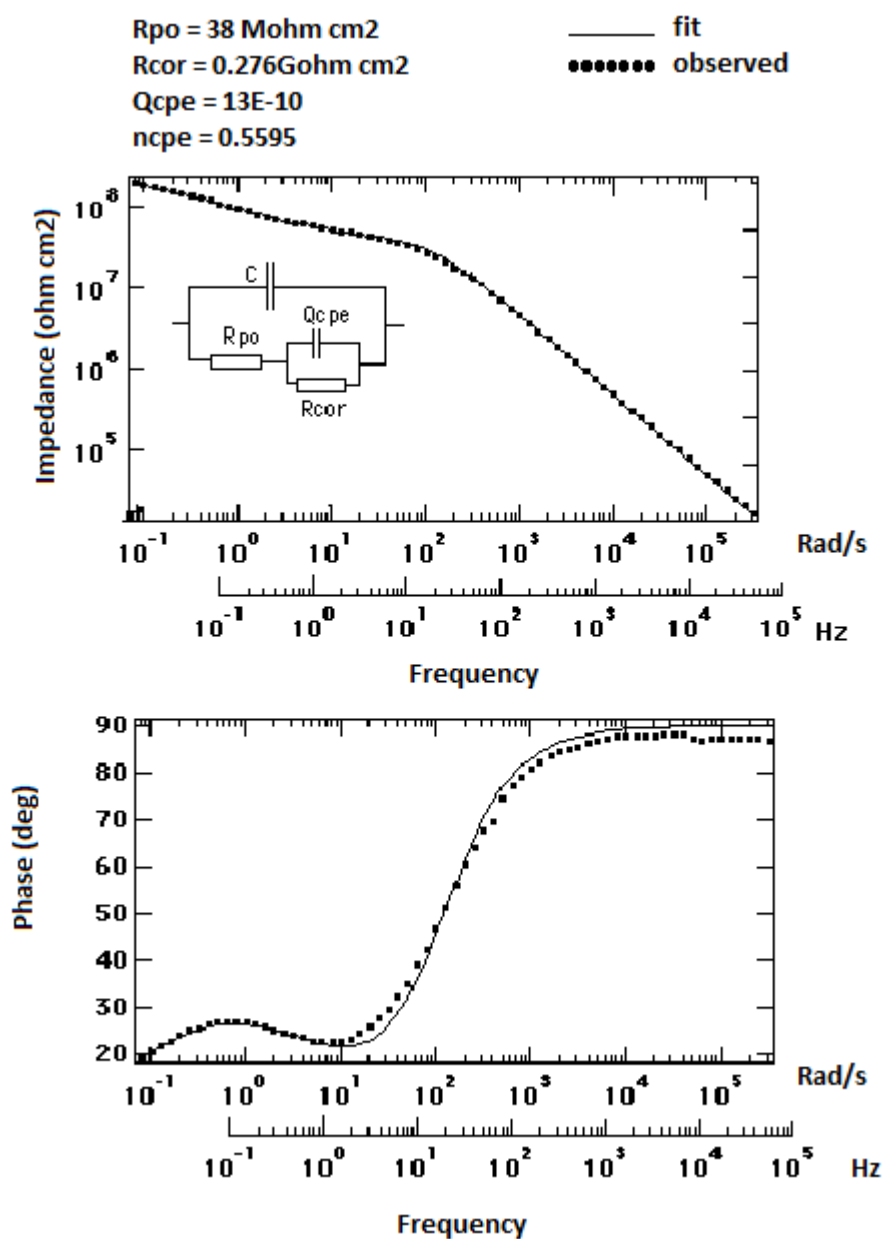


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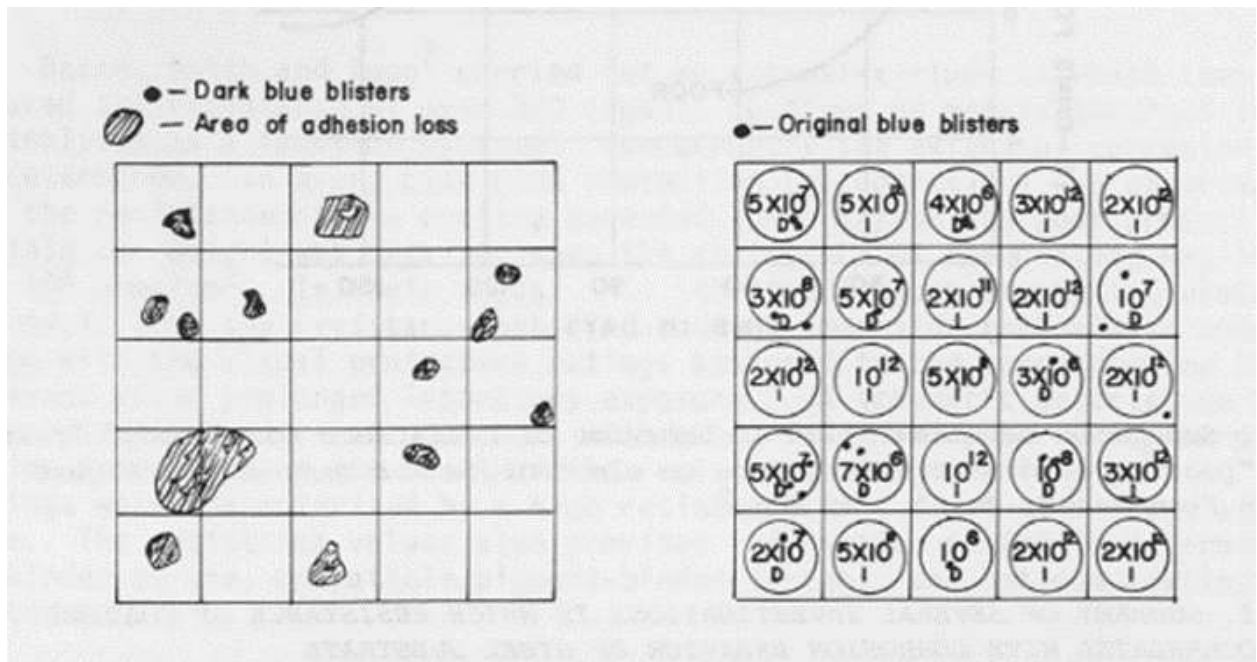


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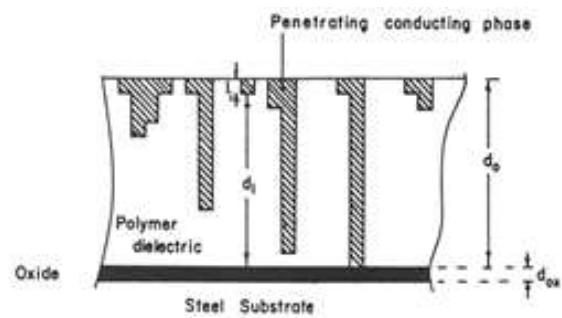


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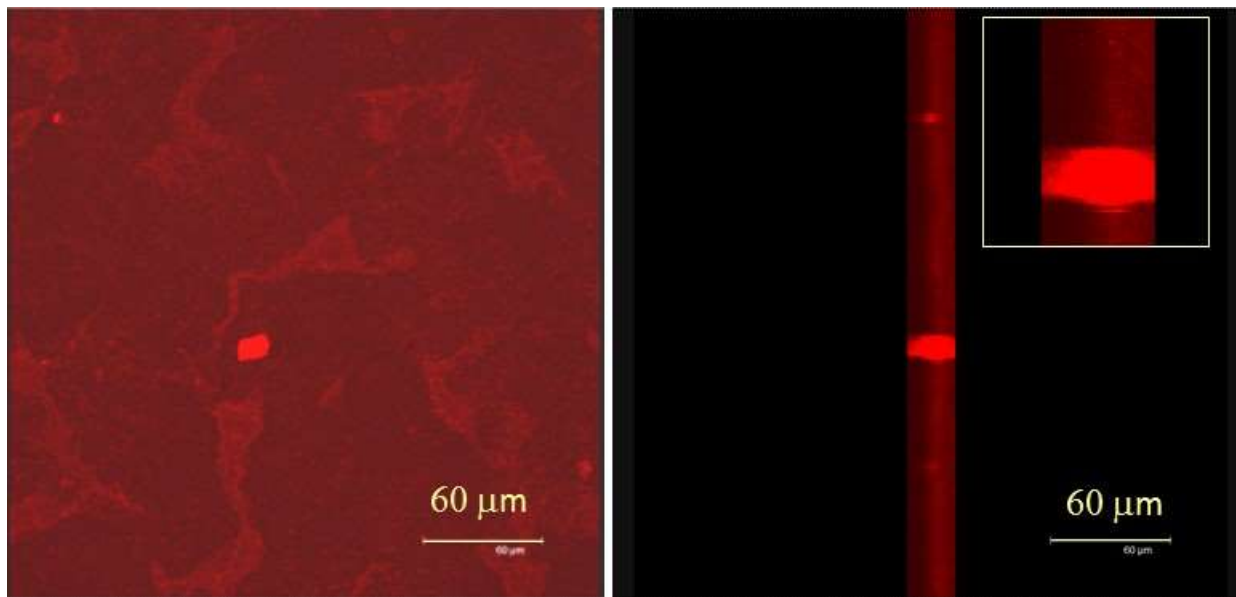


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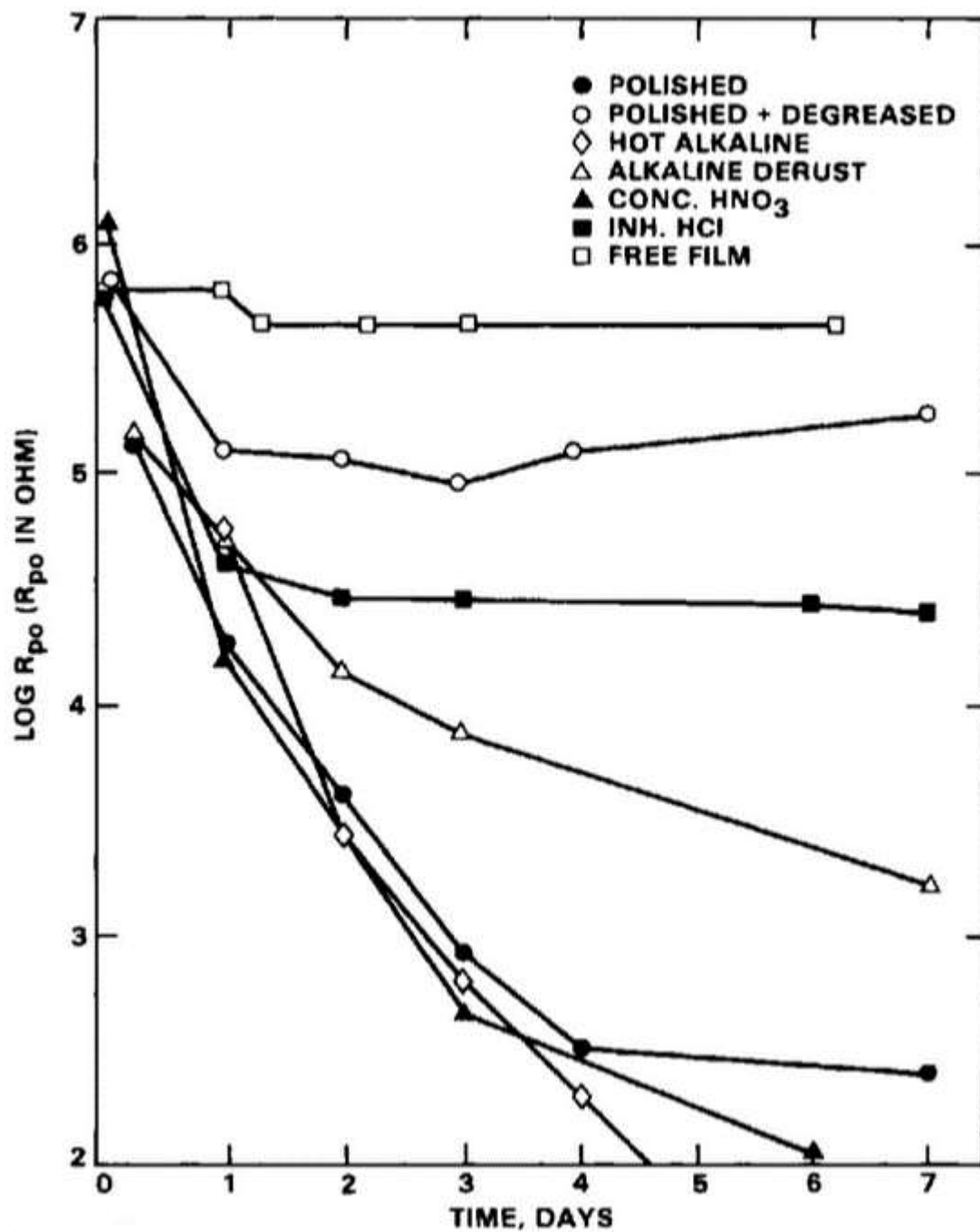


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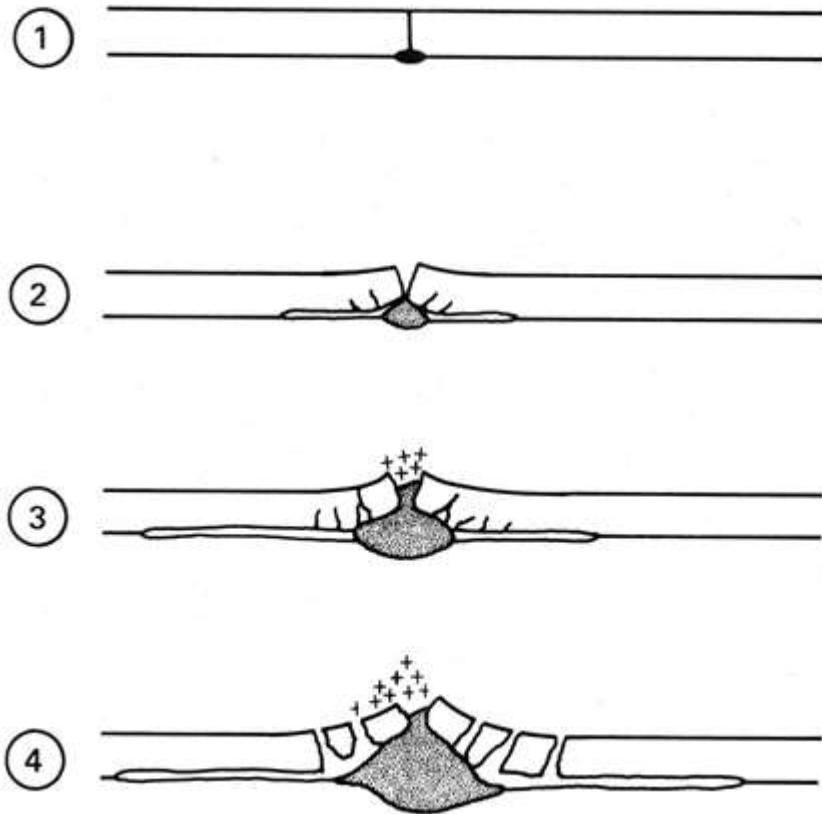


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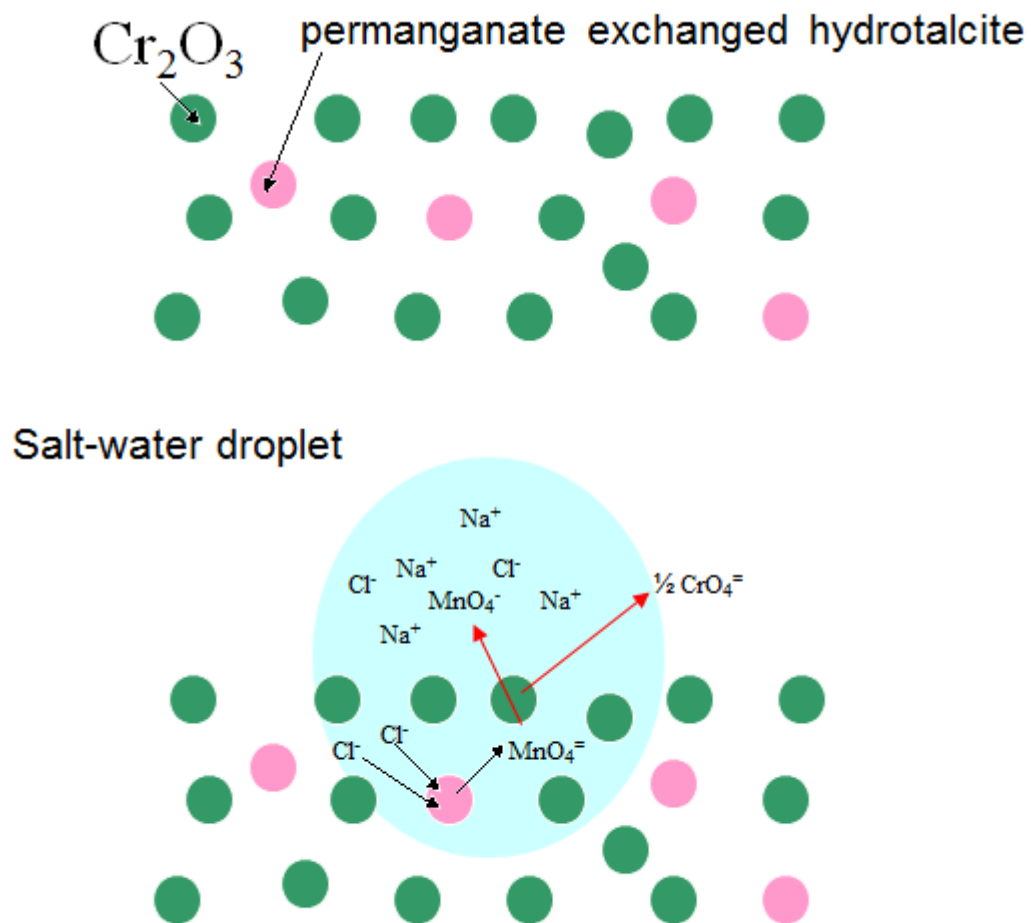


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