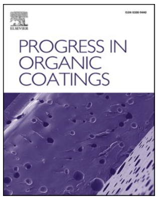
Progress in Organic Coatings 208 (2025) 109475

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat



Review

Forty years of symposia on "Advances in Corrosion Protection by Organic Coatings" and the legacy of Jack Mayne[☆]

S.B. Lyon[a,*], D.J. Mills[b]

[a] Corrosion@Manchester, Department of Materials, University of Manchester, Manchester M13 9PL, UK
[b] Department of Technology, University of Northampton, NN1 5PH, UK

ARTICLE INFO

Keywords:
Organic coatings
Corrosion protection
Mechanisms
Heterogeneity

ABSTRACT

In 1986, believing that the subject discipline needed more attention, Henry Leidheiser (Lehigh University, Pennsylvania, USA) and Martin Kendig (Leidheiser's former PhD student) organised a focussed research meeting on corrosion protection by organic coatings at the 1986 Fall meeting of The Electrochemical Society. In 1989 David Scantlebury (University of Manchester, UK) organised a further meeting in Cambridge entitled "Advances in Corrosion Protection by Organic Coatings" (ACPOC). Subsequent meetings have been held roughly quinquennially in Cambridge, Tokyo and Manchester with the latest (the 10th) held in Tokyo in 2024. This contribution takes inspiration from the outputs of Dr. J.E.O. (Jack) Mayne in Cambridge (UK) working from 1955 to 1980 who, in turn, was the inspiration for establishment and continuation of the ACPOC meeting series by Mayne's former students and colleagues. We provide an historical survey of research on corrosion protective organic coatings prior to and arising from Mayne's work and highlight key findings presented at ACPOC symposia, including the continued relevance of coating heterogeneities as initially characterised by Mayne.

1. Introduction

Over last 40 years there has been a huge increase in research outputs on corrosion protective organic coatings as can be readily demonstrated with bibliographic searching. For example, Table 1 shows 10-year fractions of outputs (and citations of those outputs) selected from the Scopus database using the keywords "paint" and "corrosion protection"; alternate keywords were found to produce similar results.

The upturn in both number of publications, and citations to those publications, from the mid-1970s onwards is remarkable. The table also reveals the disparity between recent, relatively well-cited works to earlier and very poorly cited work from 50 or more years ago. During the last half-century many advances have been made the use of novel materials in the development of higher-performing protective coatings. For example, advances include the introduction of nanomaterials [1] and 2-D materials [2,3], bio-inspired materials [4], smart self-healing coatings [5,6] and coatings based on metal-organic frameworks [7]. There are increasing requirements for more environmentally friendly materials with life cycle costing needed to identify the most sustainable materials [8].

This paper provides an historical survey of the establishment of corrosion protective coatings as a valid topic for scientific endeavour arising largely through the works of Mayne in the UK.

2. Background

2.1. Historic observations and phenomenology

Corrosion of iron, and some means for its protection, were first described by Pliny the Elder in his Natural Histories [9]: "… (*iron) can be protected from rust by means of lead acetate, gypsum and tar; rust is called by the Greeks 'anti-pathia' or the 'natural opposite' to iron.*" Historically observation of corrosion damage was entirely phenomenological and the realisation of how metals corrode, and how to prevent corrosion, has only gradually developed over the last 200 years. Today we can see that Pliny's reports are mechanistically consistent with lead salts inhibiting rusting, gypsum leaching calcium ions providing a cathodic inhibitor, and organic coatings of tar/pitch providing a physical barrier to the environment.

Since 1834 Faraday's laws of electrolysis had underpinned the basic

---

[☆] This article is part of a Special issue entitled: 'ACPOC2024' published in Progress in Organic Coatings.

[*] Corresponding author.
E-mail address: stuart.lyon@manchester.ac.uk (S.B. Lyon).

https://doi.org/10.1016/j.porgcoat.2025.109475
Received 29 April 2025; Received in revised form 16 June 2025; Accepted 17 June 2025

Table 1
Decadal publication and citation percentages for search terms "paint" + "corrosion protection" (Scopus).

	Publications	Citations
2016 to 2025	21.7 %	19.0 %
2006 to 2015	25.3 %	42.6 %
1996 to 2005	20.5 %	23.9 %
1986 to 1995	15.2 %	11.1 %
1976 to 1985	12.6 %	2.2 %
1966 to 1975	3.7 %	1.1 %
≤1965	0.5 %	<0.01 %

electrochemistry of metal dissolution [10], but corrosion damage was long held to be caused by "chemical agents" such as acids (including carbonic acid) and hydrogen peroxide [11]. A more detailed understanding of the corrosion process was not possible until the concept of solutions and electrochemical potential were developed by Ostwald and Nernst [12]. This enabled Whitney in 1904 to state boldly that [13]: *"If we now apply Nernst's conception of the source of electromotive force between a metal and solution we must conclude … the whole subject of corrosion of iron is an electrochemical one and the rate of corrosion is simply a function of electromotive force and resistance of circuit."* In 1908, Walker et al. also recognised the importance of oxygen in corrosion reactions and that potential differences were present on corroding metal surfaces [14]; *"… the rapidity of corrosion in water is a linear function of the partial pressure of oxygen … areas having a marked difference in potential exist upon the surface of a piece of iron prone to corrosion"*.

Traditional organic coatings, generally comprising drying oils, tar binders, etc., have been used to protect against corrosion for many thousands of years. However, the underpinning scientific tools and knowledge to understand how such materials work on a mechanistic basis was entirely absent. Indeed one of the earliest textbooks on organic coatings by Friend in 1910 focusses on the chemistry of pigments and binders but largely ignores their function [15]. This gap in knowledge was identified by Toch in 1915 who noted [16]: *"A careful search of the literature of the past twenty years has failed to reveal anything like a systematic investigation of the relative value of different vehicles used in the manufacture of paints for structural steel and the prevention of corrosion"*.

It was generally assumed (but not proven) that protective coatings functioned mainly by excluding the environment from the substrate with Edwards claiming: *"the ability of a paint to exclude moisture is one of its most important functions"* [17]. Consequently, much historic fundamental research on paint performance was concerned with determining coating permeability and how this varied with pigment type, pigment loading, and type of vehicle (binder) [18,19]. By 1935 the importance of substrates was becoming appreciated particularly in the automotive and aircraft industries where paint performance was linked to surface preparation and cleanliness. Also, the use of conversion coatings (e.g. phosphating/chromating) to increase paint adhesion was becoming prevalent. In this way adhesion, in addition to permeability, became accepted as the two most important factors influencing performance [20,21]. However, even after the electrochemical theory of corrosion began to be widely promoted, particularly by Evans [22], the action of corrosion inhibitive pigment was often interpreted in terms of obsolete ideas with Nelson stating, erroneously: "*Pigments that give effective service in metal priming paints apparently are those which neutralize acids and reduce or otherwise decompose hydrogen peroxide*" [23]. Nevertheless by 1939, practical experience had led to Rassweiler describing how to optimise the process of painting [24]: "*The successful protection of steel with organic coatings requires careful attention to four factors:* 1. *selection of material; 2. surface preparation; 3. correct application; and 4. adequate film thickness*". All of these elements are still regarded today as of critical importance.

2.2. Hypotheses and the scientific method

Polymers, generally having high electrical resistance, were historically used to insulate, for example: motor and transformer windings (lacquers) and cabling (rubber and bitumen). Using this idea, in 1911 Benson and Pollock [25] suggested that the charge passed between painted electrodes at different potentials in salt solution might provide a proxy measure of paint lifetime. Unfortunately, their method was not successful as the large potential difference used prematurely destroyed the materials. A more considered approach was adopted in 1936 by Burns and Haring [26] who measured the electrochemical potentials of coated steel immersed in sodium chloride solution with pigmented paints. Systems containing iron oxide maintaining a relatively negative (active) potential while those with red lead developed a much more positive potential indicating that passivation of the substrate had occurred. However, despite their promising ideas, both papers were largely ignored. Unfortunately, the application of electrical measurements to study the performance of coatings had to wait a further decade until two papers were published within a few months of each other in the UK and the USA.

In 1947 Wormwell and Brasher [27] correlated the capacitances, resistances, potentials and areas of rust for variously pigmented paint films on steel as a function of time of immersion in salt solution, Fig. 1. These data showed, for the first time, that as such coatings degraded (i.e. the area rusted increased), the coating resistance decreased, and capacitance increased.

Shortly afterwards, Bacon, Smith and Rugg [28] published their results of over 300 samples, varying pigment, coating thickness and external salt concentration. By tracking the resistance of coatings in salt solutions over 150 days they determined that good protection was afforded where the coating resistance exceeded 10^8 Ω/cm^2, and poor performance when $<10^6$ Ω/cm^2. Resistances between these values only provided a fair, or intermediate, degree of protection (Fig. 2).

Together these two papers essentially kick started scientifically-based studies on protective organic coatings. They prompted Mayne, in 1954, to apply the electrochemical theory of corrosion in interpreting how paints work [29]. He noted that the average corrosion rate of bare (uncoated) iron in the atmosphere was about 100 $\mu m\ yr^{-1}$ from which the required consumption rate of water and oxygen to form various oxides of iron can be calculated and compared with the permeation rates of water and oxygen through paint binders, Table 2.

From this Mayne concluded that: *"… paint films are so permeable to water and oxygen that they cannot inhibit corrosion by preventing the reactants reaching the surface. That is to say they cannot inhibit the cathodic reaction"*. This left two possibilities for how paints work: passivation of the anodic reaction and resistance polarisation.

Anodic passivation of iron, that is the formation of a protective film on the metal surface underneath the coating, was understood to occur either by using a soluble inhibitive pigment such as a chromate [30] or via the pigment reacting with the binder/vehicle to form an inhibitive metal soap such as lead linoleate (e.g. from lead carbonate dispersed in linseed oil) [31]. Alternatively, coatings that provide significant protection in the absence of inhibitive pigments must do so via the resistance of the coating. Kittleburger and Elm measured the ionic resistance of polymer using a two compartment cell. Changes in chloride concentration across the membrane separating the two compartments, determined by potential changes using chloride sensitive electrodes, confirmed that the ionic diffusion rate was 1000 to 100,000 times smaller than the water permeation rate [32]. Together, these insights allowed Mayne to provide the first robust scientific interpretation of Bacon, Smith and Rugg's observations.

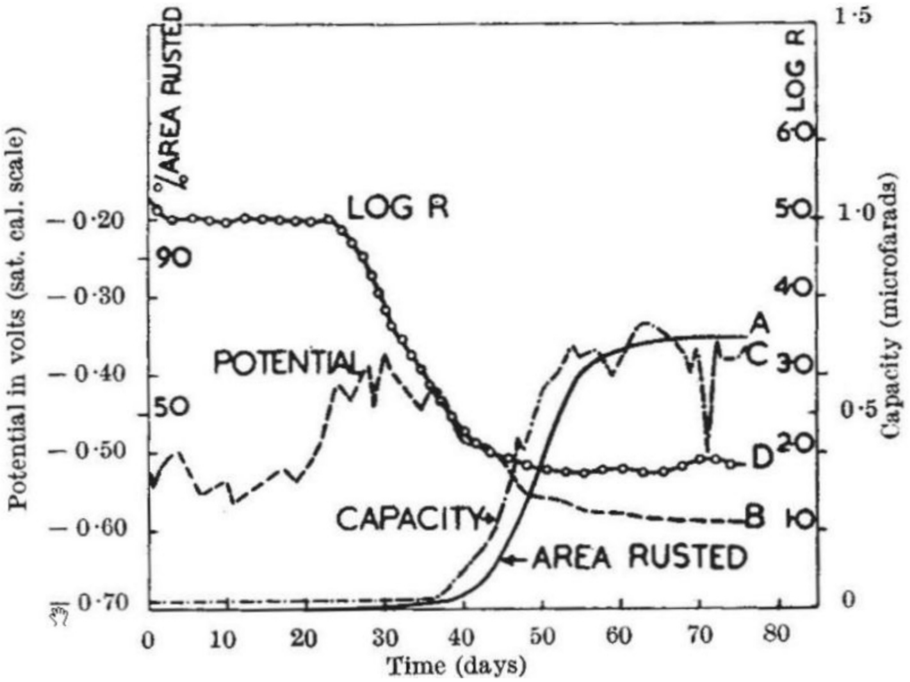


Fig. 1. Relationship between area rusted and changes in electrical properties of paint films on steel ([19] with permission).

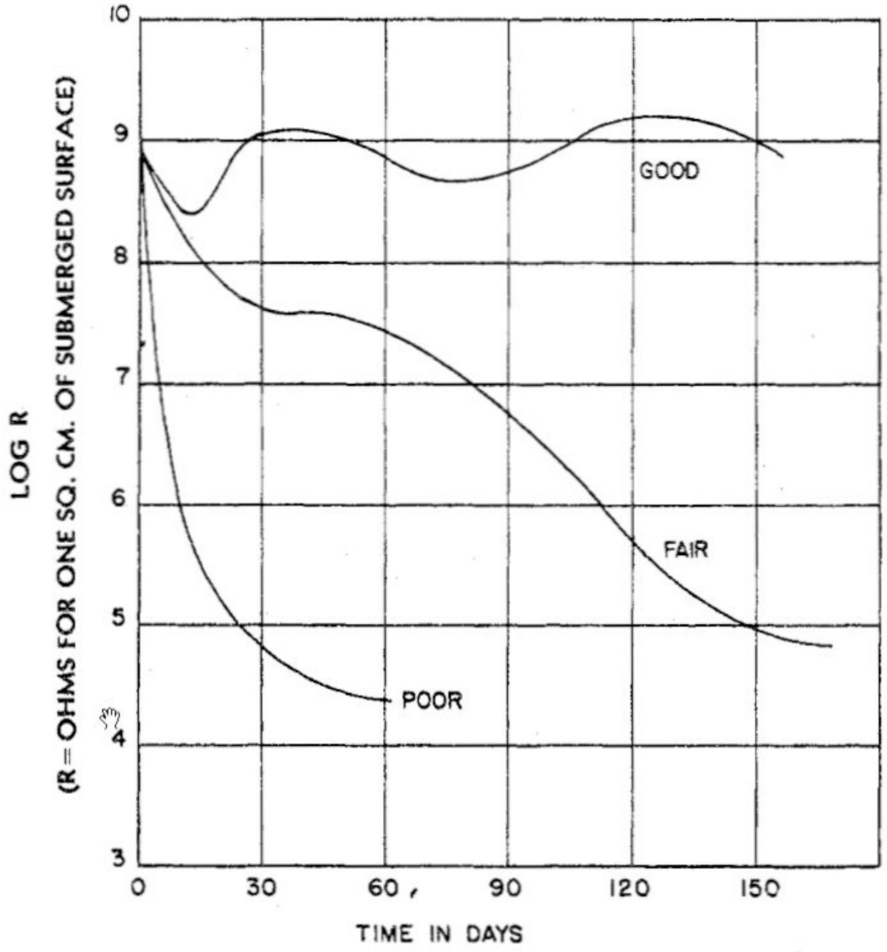


Fig. 2. Schematic resistance behaviour of coatings on immersed metals ([20] with permission).

Table 2
Correlations between corrosion rate, consumption rates of reactants and permeations rates through coatings, after [21].

Substrate	Corrosion rate
Uncoated iron	100 μm yr^{-1}/78.6 mg cm^{-2} yr^{-1}

Oxide	Required consumption rate of reactants
$Fe_2O_3 \cdot H_2O$	12.4 mg H_2O cm^{-2} yr^{-1} plus 33.7 mg O_2 cm^{-2} yr^{-1}
$Fe_3O_4 \cdot H_2O$	8.9 mg H_2O cm^{-2} yr^{-1} plus 30.3 mg O_2 cm^{-2} yr^{-1}
FeOOH	25.8 mg H_2O cm^{-2} yr^{-1} plus 22.5 mg O_2 cm^{-2} yr^{-1}

Coating	Permeation rate of reactants through 100 μm
Polystyrene	545 mg H_2O cm^{-2} yr^{-1} plus 14.6 mg O_2 cm^{-2} yr^{-1}
Asphalt	213 mg H_2O cm^{-2} yr^{-1} plus 59.5 mg O_2 cm^{-2} yr^{-1}

3. Mayne and his contemporaries

3.1. Mechanistic understanding

From the mid 1950's to the 1980s Mayne supervised a series of research students at Cambridge who conducted systematic sequence of investigations on unpigmented and pigmented free (or unattached) films, and varnish and pigmented coatings on steel. Although ionic resistance of the film was the main property of interest other properties, including the influence of film glass transition temperature, water uptake, external ionic strength and the influence of inhibitive pigments were also considered. He reviewed findings in 1970 [33] with major discoveries including: electrochemical heterogeneity in the polymer on a scale similar to the thickness of a typical coating, the relative unimportance of adhesion above a minimum level and the fact that the polymers used in coating films could undergo reversible ion exchange.

Mayne's team used DC polarisation to measure film resistances in a method similar to that of Kittelburger and Elm. Films were cast at consistent thickness onto glass plates, then detached and placed as the membrane between a two compartment electrochemical cell. Two distinct forms of behaviour were identified. The most common is where the film resistance varies proportionately with the external solution concentration ("D" type), Fig. 3. However, some films showed the opposite behaviour where the resistance varied inversely with external concentration ("I" type). The resistance of "I" type films was determined to be independent of solute (i.e. whether ionic or not) and hence was related to the external water activity which controlled the amount of water in the film at equilibrium, Fig. 4. Generally in solutions with ionic activity equivalent to sea water (eg 0.6 M NaCl) 1 cm^2 areas, "I" type areas had DC resistance three or four orders of magnitude greater than similar size "D" type areas.

The experimental concept was adapted to map out "D" and "I" areas over much larger areas of detached film and demonstrated clear inhomogeneity with adjacent 1 cm^2 areas showing different behaviours. Thus, when exposed to 3.5 M KCl, unpigmented films on steel prepared from three binders (pentaerythritol-alkyd, tung-oil phenol formaldehyde and epoxy-polyamide) broke down revealing rust spots within one week at room temperature [34]. Regions of adhesion loss corresponded to "D" areas while "I" areas all remained intact, Fig. 5. This was the first demonstration of significant inhomogeneity within cross-linked binders and prompted the conclusion: "*… in unpigmented lacquer films, cross linking is very uneven and films with greatly improved protective value would be produced if cross linking could be rendered more homogeneous*".

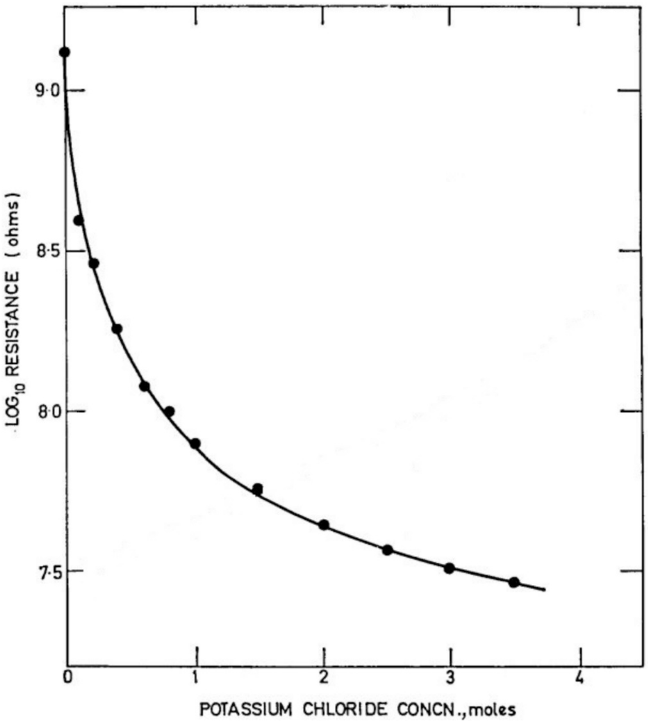


Fig. 3. Variation in coating resistance to the external solution concentration: ● - "D" type films (after [33], with permission).

At this time corrosion protective coatings were still largely using alkyd and drying oil binders. Consequently, the formation of metal soaps by reaction between inhibitive pigments (e.g. red lead, zinc oxide, calcium carbonate, etc.) and fatty acids was considered to be the dominant mechanism of inhibition. Also, compared with coatings containing more soluble pigments, e.g. zinc chromate, the low solubility of oxide pigments ensured that coatings did not develop significant porosity which was seen to be an advantage. However, the gradual introduction of lead-free coatings with more modern binders such as epoxies, was changing this paradigm. For example, zinc phosphate, which did not form metal soaps, was found to have excellent performance albeit with very low solubility, so its protective mechanism fell outside the theory [35].Other advances in understanding were occurring. The significance of coatings as environmental barriers was being reassessed by Funke and others, who also championed adhesion as one of the primary mechanisms of protection: "*Wet-state adhesion and water and oxygen permeability are inherent film properties which determine the corrosion protective capability of paint systems*" [36]. Analytical tools and electrochemical instrumentation were becoming cheaper to acquire and experiments easier and quicker to accomplish in the laboratory. Leidheiser and Kendig were early proponents of the application of electrochemical impedance which demonstrated that when the coating resistance "*… falls below 10^6 to 10^7 ohms cm^{-2}, corrosion beneath the coating is occurring at a significant rate*" [37,38] thus agreeing with Bacon, Smith and Rugg's measurements some 30 years earlier. Researchers were also considering the mechanisms for coating delamination and blistering. Leidheiser demonstrated that the area of coating delamination was proportional to cathodic charge passed, Fig. 6, consistent with the hypothesis that alkalinity at cathodic areas caused adhesive failure of the coating [39]. Mayne's former student, Scantlebury, applied zero resistance ammetry to demonstrate the development of cathodic and anodic areas adjacent to blisters in coatings, further supporting this hypothesis [40].

The then state-of-the-art was reviewed by Walter in 1986 who summarised the previous forty years of research [41]. He pointed out that the introduction of more advanced tools, particularly electrochemical impedance, had revolutionised the study of protective coatings. Modern, much higher performing, polymer binders were also being introduced at this time which required better, more discriminating, and more rapid methods for laboratory assessment. Corrosion protection by paint could provide protection by resistance polarisation (high electrical

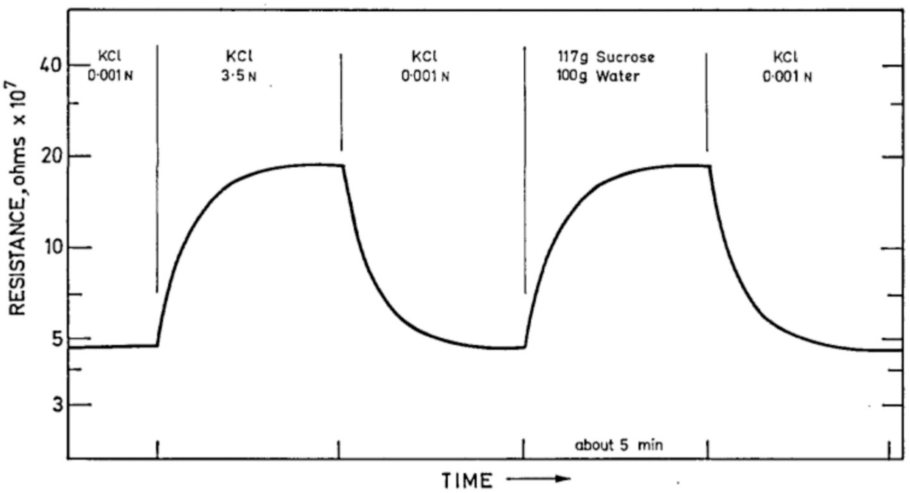
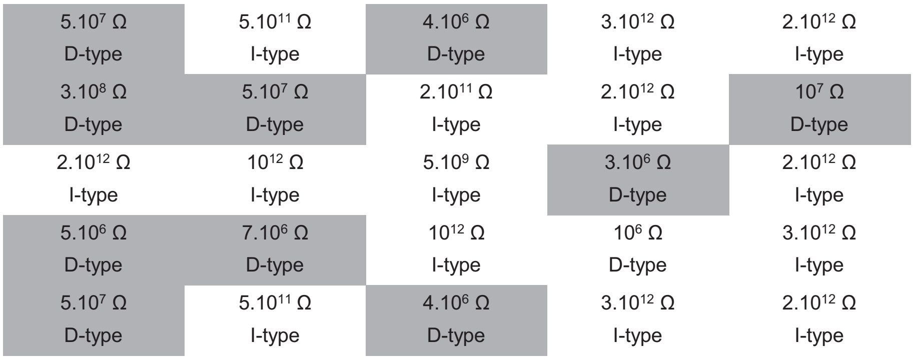


Fig. 4. Effect of concentration and solute on an "I" type film ([33] with permission).



5.10^7 Ω D-type	5.10^{11} Ω I-type	4.10^6 Ω D-type	3.10^{12} Ω I-type	2.10^{12} Ω I-type
3.10^8 Ω D-type	5.10^7 Ω D-type	2.10^{11} Ω I-type	2.10^{12} Ω I-type	10^7 Ω D-type
2.10^{12} Ω I-type	10^{12} Ω I-type	5.10^9 Ω I-type	3.10^6 Ω D-type	2.10^{12} Ω I-type
5.10^6 Ω D-type	7.10^6 Ω D-type	10^{12} Ω I-type	10^6 Ω D-type	3.10^{12} Ω I-type
5.10^7 Ω D-type	5.10^{11} Ω I-type	4.10^6 Ω D-type	3.10^{12} Ω I-type	2.10^{12} Ω I-type

Fig. 5. Schematic of coating on steel divided into 1 cm^2 areas showing corrosion spots. The DC resistances of all areas are correlated with visible rust; shaded areas have failed and are all "D" type, intact areas are all "I" type (after [33]).

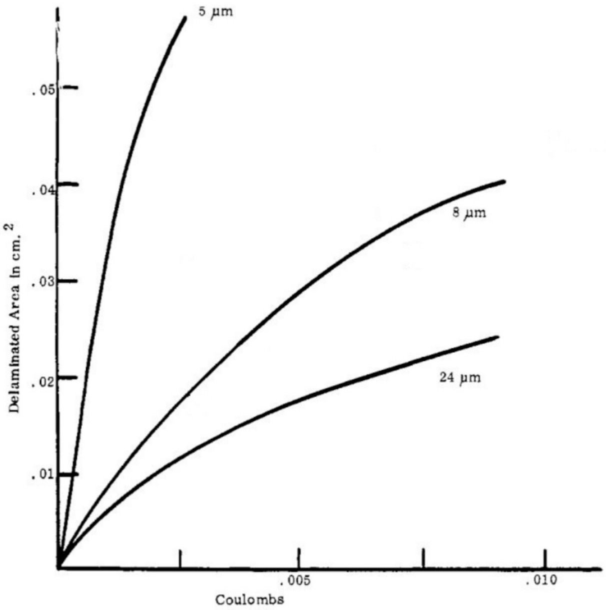


Fig. 6. Variation in delaminated area with charge passed during cathodic treatment ([39] with permission).

resistance of the film), cathodic polarisation (restricted permeation of cathodic reactants through the film) and concentration polarisation of the anodic reaction (limited migration of metal ions outwards from the metal coating interface and passivation). The longevity of paint coatings tended to reflect the reactivity of the substrate with coatings on aluminium and zinc generally lasting longer than the same coatings on steel. Such differences were ascribed to adhesion of the coatings and their tendency to blister. Mayne's hypothesis that paints were not impermeable membranes had been confirmed with neither water, nor oxygen permeation generally thought to be rate-limiting factors in under-film corrosion.

Environmental uptake into coatings could be followed by changes in DC resistance or AC impedance and involved a two-stage process. Initially ingress of the external aqueous environment was relatively rapid then a slower process involved internal changes and deterioration of the coating structure and at the coating metal interface. Water uptake into coatings was largely dependent on the external water activity (osmotic pressure) which affected the tendency to blister, Fig. 7. Generally it was found that the diffusion of anions and cations was found to be so small as have negligible influence on substrate corrosion rate while water diffusion could lead to loss of adhesion. Overall, Walter summarised that while many findings could be generalised: "*the multi-faceted problem of why paint films protect metals has still to be clarified*" and that "*the diversity of paint types ... is certain to result in more than one degradation mechanism*".

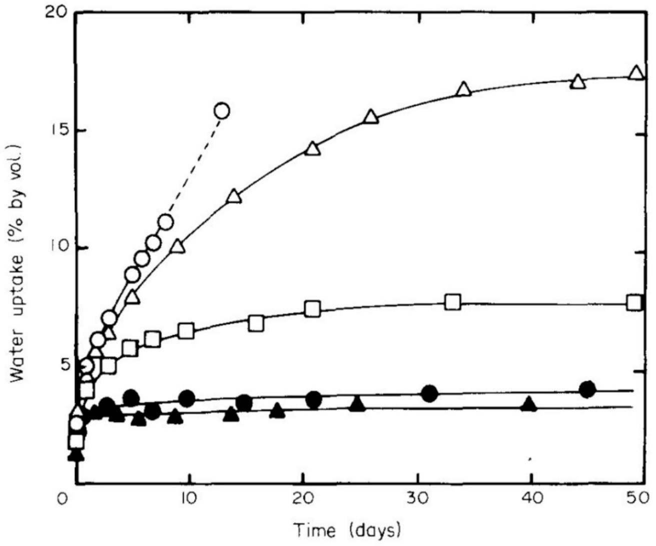


Fig. 7. Water uptake of painted steel panels in sucrose solutions of varying molality/osmotic pressure: 0.1 M (open circles), 0.5 M (open triangles), 1 M (open squares), 2 M (filled circles), 3 M (filled triangles). ([42] with permission).

4. Advances in Corrosion Protection by Organic Coatings

The first few symposia on "(Advances in) Corrosion Protection by Organic Coatings" were held under the auspices of The Electrochemical Society in 1986 (San Diego), 1989 and 1994 (Cambridge) and 1997 (Tokyo) with proceedings volumes issued for the 1986, 1989 and 1997 meetings [43–45]. The majority of papers presented at these meetings fell into the following main categories: corrosion mechanisms and transport processes, adhesion and surface preparation, new electrochemical approaches, alternative tools such as microscopy and surface analysis, novel types of coating, novel pigment systems including inhibitors, and performance in service.

A dominant theme of the first meeting was coating adhesion and, conversely, loss of adhesion due to blistering and disbonding. Much attention was paid to the mechanism(s) of cathodic delamination and, in particular, how the rate changed as a function of the external medium. An interesting paper by Watts, Castle, Mills and Heinrich applied surface analytical tools (X-ray photoelectron spectroscopy and Rutherford backscattering) to analyse the locus of failure of disbonded polybutadiene films [46]. They found residual polymer present on the metal which was the first indication that delamination might occur within an interphase region.

By the 2rd meeting attention had turned to the control of under-film corrosion using inhibitors and other additives. Looking backwards, Thomas [47] sought to elucidate why red-lead containing alkyd paints had such good anti-corrosion performance on rusty steel. She found that barrier properties were far inferior to systems containing aluminium flake. Lead also does not form sulfates within the metal-rust-polymer interfaces as no correlation between Pb and S was found in high resolution analytical microscopy. However lead was found at low levels within the rust layer where it was likely to be inhibiting the redox reactions of iron oxides during wet and dry environmental cycles. In contrast a leap forward came from the paper by Agarwala, de Luccia and Bailin [48] who presented an early form of self-healing "smart" coating where an inorganic corrosion inhibitor was micro-encapsulated within a polymer shell and then dispersed into an epoxy coating. The capsules were designed to release inhibitor when the coating suffered physical damage thus inhibiting corrosion on demand.

The 4th meeting, held in Japan, focussed more on coating performance in applications with papers on coil-coatings, coatings for structural steel and pipeline coatings. Research papers included Mills and Mabbutt [49] who introduced a novel method to study coating inhomogeneities using electrochemical noise. Novel surface treatments (silanes and electropolymers) were suggested as replacements for conventional chromating and phosphating. Van Ooij [50] reported that optimisation of the silane treatment resulted in performance as good as, or better than, conventional surface treatments, Fig. 8.

The 5th to 8th meetings were all held in Cambridge being similar in scope to previous meetings, and again attracting papers on mechanisms of failure, new surface treatments, and novel investigative methods. Highlights of the 5th meeting include Knudson and Steinsmo who applied detailed analytical microscopy to confirm that Al-flake pigmented marine coatings are resistant to disbonding under applied cathodic protection. This was because of the consumption of aluminium by the cathodically generated alkalinity thus buffering the under-film pH [51]. In the 6th meeting nanomaterials were beginning to be identified for use in coatings with Greenfield and Clegg exploring the use of exfoliated clays in reducing the transport of water and oxygen through coatings [52]. In the next meeting Sykes and Yu promoted considerable discussion as they revisited the hypothesis that protective coatings controlled corrosion by resistance polarisation of the electrochemical reactions [53]. By using coupled zinc and steel bi-electrodes they demonstrated that, even in the case of coatings with high ionic resistance, the ohmic potential drop in the coating is often less important in regulating corrosion rate than the polarisation of the anodic reaction.

The then state-of-the-art was briefly summarised in the 8th meeting by Kendig and Mills [54] who concluded that the following four factors controlled corrosion protection by coatings and, notwithstanding the significant advances in the previous 50 years, still required further study:

- whether the ionic resistance of the paint coating, which decouples the anode and the cathode reactions, is always dominant,
- the extent to which the coating provides a platform for holding corrosion inhibitive pigments and for the transport of inhibitive species,
- limits on corrosion protection resulting from the nature of heterogeneities,
- the limits to wet adhesion under conditions of corrosion and in the presence of wet environments.

Due to COVID restrictions the 9th ACPOC meeting, originally scheduled for 2020, was delayed until 2021 and then held as a hybrid event. Delegates attended Manchester under social distancing rules while the event was also streamed to a wider online audience. The defining characteristic of this meeting was the huge advance in materials modeling using finite element, cellular automata and molecular dynamics approaches coupled with experimental verification using high resolution analytical microscopies including 3D tomographic visualisation and infra-red analysis using atomic force microscopy (AFM-IR).

Referring directly back to, and inspired by, Mayne's observations on "D" and "I" areas in paint coatings, Morsch reviewed her recent work on network polymers using the AFM-IR method to spectroscopically map coating surfaces at the nanoscale. She concluded that heterogenous nanostructures are an intrinsic feature of epoxies with water uptake proceeding in a heterogenous manner. However, water uptake leads to plasticisation and long-term re-arrangement of the network such that overall water uptake is determined by degree of cross-linking. Jamali and Mills determined the "D" and "I" percentages for various coating types and thicknesses, Fig. 9. They concluded that a continuous conducting pathway is essential for "D" type films and that such a pathway becomes more unlikely as the coating thickness increases. However, waterborne coatings maintain "D" type behaviour irrespective of thickness due to intrinsic continuous pathway between latex particles.

Supporting this assessment, Wand demonstrated a molecular dynamic model of epoxy-amine systems with varied cross-link density

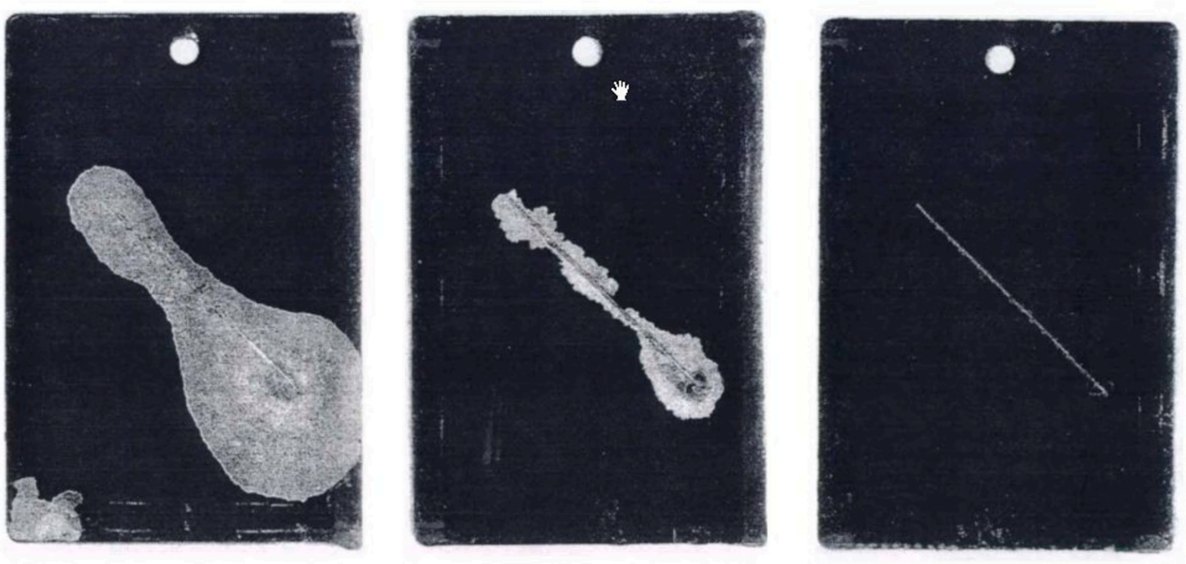


Fig. 8. Polyurethane coated galvanised steel after corrosion testing: (left) alkaline etched only, (centre) phosphated, (right) silane treated ([50] with permission).

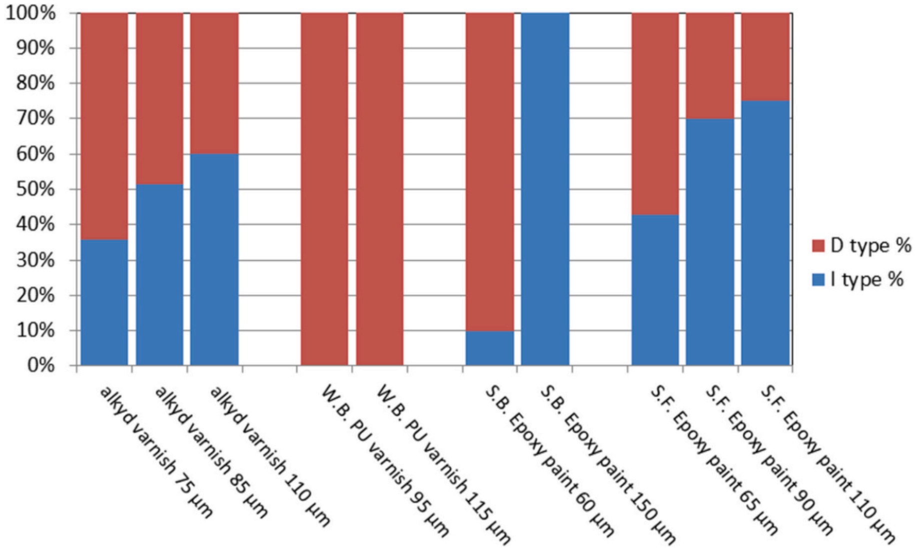


Fig. 9. Percentage “D” and “I” type films, 1 cm^2 in area, for different types and thickness of paint coatings.

which he used to explore network heterogeneity and diffusion of water [55]. He showed that 50 % cross-linking produces a much larger proportion of available pores (free volume) in the polymer network compared with near complete (98 %) cross-linked networks. Significantly, this translated to an inverse relation between diffusion coefficient and polymer cross-link density, Fig. 10. Seventy years after Mayne’s original ideas these works validated the importance, and confirmed the continued relevance, of his key hypothesis linking coating heterogeneity to service performance of corrosion protective organic coatings.

5. Concluding remarks

The main purpose of an anti-corrosive coating is to provide conditions at the paint metal interface which are conducive to restriction of the anodic reaction. This may be achieved by one or more of: the ionic and electronic resistance of the polymer coating, concentration polarisation restricting the solvation of metal ions, formation of a stable oxide film via passivation, or through the action of chemical inhibitors leached from pigments. Mayne was the first to apply these testable, mechanistic, hypotheses to protective organic coatings and corrosion inhibitive pigments using (for the time) innovative experimental methods underpinned by a belief in electrochemistry. He tutored, mentored and inspired a generation of UK and overseas scientists. His core research legacy remains the concept that heterogeneity within polymer networks leads to measurable differences in local transport properties giving rise to local regions of coatings with measurably different properties. Although not fully testable when first postulated, the tools now exist to model, experimentally probe and validate, the detail of his ideas at the length scales required.

CRediT authorship contribution statement

S.B. Lyon: Writing – original draft, Conceptualization. **D.J. Mills:** Writing – review & editing, Conceptualization.

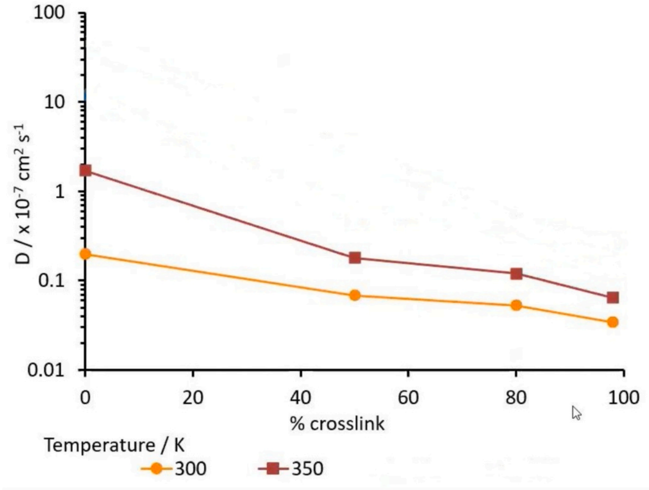


Fig. 10. Molecular modeling of the diffusion coefficient for water in epoxy amine systems as a function of cross-link density [55].

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Until retirement in 2024, Stuart Lyon was Editor-in-Chief of Corrosion Engineering Science and Technology and AkzoNobel Professor of Coatings Technology (University of Manchester, UK), receiving research funding from AkzoNobel. Stuart Lyon and Douglas Mills are guest editors for this APCOC2024 special issue in Progress in Organic Coatings. There are no other potentially competing interests to disclose.

Data availability

No data was used for the research described in the article.

References

[1] S. Thomas, J.S. George (Eds.), Polymer-based Nanoscale Materials for Surface Coatings, pub. Elsevier, 2023.
[2] A. Dashan, S. Montazeri, S.A. Haddadi, B. Ramezanzadeh, Y. Qiang, T. H. Mekonnen, Dual-functional smart anti-corrosion coating based on $Ti_3C_2T_x$-Mxene/Zr-UIO-66- NH_2 reinforced epoxy, Prog. Org. Coat. 206, #109338 (2025).
[3] J.S. George, P. Vijayan P., K. Paduvilan, N. Salim, J. Sunarso, N. Kalarikkal, N. Hameed, S. Thomas, Advances and future outlooks in epoxy/graphene composites for anti-corrosion applications, Prog. Org. Coat. 162, #106571 (2022).
[4] J.S. George, P. Vijayan P., A.T. Hoang, N. Kalarikkal, P. Nguyen-Tri, S. Thomas, Recent advances in bio-inspired coatings for corrosion protection, Prog. Org. Coat. 168, #106858 (2022).
[5] H. Pulikkalparambil, S. Siengchin, J. Parameswaranpillai, Corrosion protective self-healing epoxy resin coatings based on inhibitor and polymeric healing agents encapsulated in organic and inorganic micro and nanocontainers, Nano-Struct. Nano-Objects 16 (2018) 381–395.
[6] N. Taheri, J. Mokhtari, B. Ramezanzadeh, Amino-functionalized MXene/cyclodextrin nanoreservoir reinforced epoxy for durable dual-function active/barrier anti-corrosion coating, Prog. Org. Coat. 204 (2025) 109279.
[7] A.F. Al Hosseini, S. Zaheri, M. Karbasi, A review of corrosion resistance in steel alloys with MOF-embedded coatings, Nano-structures and nano-objects 40, #101384 (2024).
[8] A. Borgaonkar, G. McNamara, Environmental impact assessment of anti-corrosion coating life cycle processes for marine applications, Sustainability 16, #5627 (2024).
[9] Pliny the Elder, “The natural history of metals”, *Natural Histories, Book XXXIV* (ca.) 80 AD.
[10] M. Faraday, On electrical decomposition, Philos. Trans. R. Soc. 124 (1834) 77–122.
[11] J. Newton Friend, The Corrosion of iron and Steel, pub. Longmans, London, 1911.
[12] W.H. Nernst, Die Elektromotorische Wirksamkeit der Ionen, Z. Phys. Chem. 4 (1889) 129–181.
[13] W. Whitney, The corrosion of iron, J. Am. Chem. Soc. 25 (1903) 394–406.
[14] W.H. Walker, A.M. Cederholm, L.N. Bent, The corrosion of iron and steel, J. Am. Chem. Soc. 29 (1907) 1251–1264.
[15] J. Newton Friend, An Introduction to the Chemistry of Paints, pub. Longmans, London, 1910.
[16] M. Toch, Paint vehicles as protective agents against corrosion, Ind. Eng. Chem. 6 (1915) 510–514.
[17] J.D. Edwards, Interpretation of moisture permeability measurements, Ind. Eng. Chem. 25 (1933) 846–847.
[18] R.I. Vray, A.R. van Vorst, Permeability of paint films to moisture, Ind. Eng. Chem. 25 (1933) 842–846.
[19] W.W. Kittleburger, Relation of permeability to moisture and durability of paint systems, Ind. Eng. Chem. 30 (1938) 328–333.
[20] F.P. Spruance, Rust-proofing and paint adherence technique analyzed, in: Society of Automotive Engineers (SAE), 1935. Technical Paper #350125.
[21] V.M. Darsey, Preparation of iron and steel for painting, Ind. Eng. Chem. 27 (1935) 1142–1144.
[22] U.R. Evans, The Corrosion of Metals, pub. Edward Arnold, London, 1924.
[23] H.A. Nelson, Metal priming paints: inhibiting qualities and influence of reactions within the paint film, Ind. Eng. Chem. 27 (1935) 35–41.
[24] C.F. Rassweiller, Protective coatings, in: Drilling and Production Practice, *pub.* American Petroleum Institute, 1939, pp. 620–627.
[25] H.K. Benson, C. Pollock, A new accelerated test for paints, Ind. Eng. Chem. 3 (1911) 670–671.
[26] R.M. Burns, H.E. Haring, Determination of the corrosion behaviour of painted iron and the inhibitive action of paints, Bell Syst. Tech. J. 15 (1936) 343–348.
[27] F. Wormwell, D.M. Brasher, Electrical properties of paint films on metals, Nature 159 (1947) 678–679.
[28] R.C. Bacon, J.J. Smith, F.M. Rugg, Electrolytic resistance in evaluating protective merit of coatings on metals, Ind. Eng. Chem. 40 (1948) 161–167.
[29] J.E.O. Mayne, How paints prevent corrosion, Anti-Corros. Methods Mater. 8 (1954) 286–290.
[30] J.E.O. Mayne, M.J. Pryor, The mechanism of inhibition of corrosion of iron by chromic acid and zinc chromate, J. Soc. Chem. Ind. 69 (1949) 1831–1835.
[31] J.E.O. Mayne, The protective action of lead compounds, J. Soc. Chem. Ind. 65 (1946) 196–204.
[32] W.W. Kittelburger, A.C. Elm, Diffusion of sodium chloride through various paint systems, Ind. Eng. Chem. 44 (1952) 326–329.
[33] J.E.O. Mayne, Paints for the protection of steel – a review of research into their modes of action, Br. Corros. J. 5 (1970) 106–111.
[34] J.E.O. Mayne, D.J. Mills, The effect of the substrate on the electrical resistance of polymer films, J. Oil Colour Chemists’ Assoc. 58 (1975) 155–159.
[35] J.D. Harrison, Protection of substrates by paint systems, Br. Corros. J. 4 (1969) 55–57.
[36] W. Funke, H. Haagen, Empirical or scientific approach to evaluate the corrosion protective performance of organic coatings, Ind. Eng. Chem. 17 (1978) 50–53.
[37] M.W. Kendid, H. Leidheiser, The electrical propertues of protective polymer coatings as related to corrosion of the substrate, J. Electrochem. Soc. 123 (1976) 982–989.
[38] H. Leidheiser, Electrical and electrochemical measurements as predictors of corrosion at the metal-organic interface, Prog. Org. Coat. 7 (1979) 79–107.
[39] H. Leidheiser, M.W. Kendig, Conjectures on delamination of organic coatings by corrosion, Ind. Eng. Chem. 17 (1978) 54–55.
[40] K.R. Gowers, J.D. Scantlebury, Blistering phenomema on lacquered mild steel, Corros. Sci. 23 (1983) 935–942.
[41] G.W. Walter, A critical review of the protection of metals by paints, Corros. Sci. 26 (1986) 27–38.
[42] D.M. Brasher, T.J. Nurse, Electrical measurements of immersed paint coatings on metal. II: effect of osmotic pressure and ionic concentration of solution on paint breakdown, J. Appl. Chem. 9 (1959) 96–106.
[43] Corrosion protection by organic coatings, in: M.W. Kendig, H. Leidheiser (Eds.), Symposium Proceedings, The Electrochemical Society vol. 87-2, 1987.
[44] Advances in corrosion protection by organic coatings, in: J.D. Scantlebury, M. W. Kendig (Eds.), Symposium Proceedings, The Electrochemical Society vol. 89-13, 1989.
[45] I. Sekine, M.W. Kendig, Advances in corrosion protection by organic coatings: III, in: J.D. Scantlebury, D.J. Mills (Eds.), Symposium Proceedings, The Electrochemical Society vol. 97-41, 1997.
[46] J.F. Watts, J.E. Castle, P.J. Mills, S.A. Heinrich, The effect of solution composition on the interfacial chemistry of cathodic disbondment, in: Symposium Proceedings, The Electrochemical Society 89-13, 1989, pp. 68–83.
[47] N. Thomas, The protective action of red lead pigmented alkyds on rusted mild steel, in: Symposium Proceedings, The Electrochemical Society 89-13, 1989, pp. 451–467.
[48] V.S. Agarwala, J.J. de Luccia, L.J. Bailin, Microencapsulated crack arrestment compounds and inhibitors for organic coatings, in: Symposium Proceedings, The Electrochemical Society 89-13, 1989, pp. 437–450.
[49] D.J. Mills, S.J. Mabbutt, Inhomogeneities in organic coatings: a look at their importance to protection and new ways at detecting them, in: Symposium Proceedings, The Electrochemical Society 97-41, 1997, pp. 89–100.
[50] W.J. van Ooij, C. Zhang, J.Q. Zhang, W. Yuan, Pretreatment of metals for painting by organo-functional and non-functional silanes, in: Symposium Proceedings, The Electrochemical Society 97-41, 1997, pp. 222–237.
[51] O.A. Knudsen, U. Steinsmo, Effect of barrier pigments on cathodic disbonding part 2: mechanism of the effect of aluminium pigments, www.jcse.org 2 (2000). paper 37.
[52] D. Greenfield, F. Clegg, Enhancement of Barrier Properties in Coatings Using Nanocomposites 8, www.jcse.org, 2005 paper 8.

[53] J.M. Sykes, Y. Xu, Investigation of electrochemical reactions beneath paint using a combination of methods, in: Electrochemical Society Transactions 24, 2010, pp. 137–146.

[54] M. Kendig, D.J. Mills, An historical perspective on the corrosion protection by paints, Prog. Org. Coat. 102A (2017) 53–59.

[55] Advances in corrosion protection by organic coatings, in: 9th International Symposium, 2021. Manchester, UK, *https://www.youtube.com/playlist?list=PLM9UK6ckT5kPCZS8MqU7ZiGhs8rvhuqux*.