Advances in corrosion protection by organic coatings: what we know and what we'd like to know

[#]S.B. Lyon[1], D.J. Mills[2], R. Bingham[1]

[1] Corrosion and Protection Centre, School of Materials, The University of Manchester, Oxford Road, Manchester, M13 9PL

[2] School of Science and Technology, University of Northampton, St. George's Avenue, Northampton, NN2 6JD

[#]Corresponding author: stuart.lyon@manchester.ac.uk

Abstract

This paper provides a brief overview of current knowledge in how protective coatings work and poses questions that we need to answer in order to develop a more predictive model for coating performance.

1. Introduction

Organic coatings are the single most widely applied method for corrosion protection of metallic materials – common examples being in transport (e.g. automobiles, aircraft, ships, etc.) and infrastructure (e.g. pipelines, bridges, buildings, etc.). Protective organic coatings are complex products consisting of various discontinuous solid functional additives, commonly known as "pigments" that are contained within a continuous polymeric phase known as the "binder". Pigments contribute to functionality in the coating in a number of ways that are not always experimentally proven beyond doubt. For example: corrosion inhibition by sparingly soluble species leached from pigments (for which there is good support) and a pigment barrier effect that excludes the external environment (for which there is more limited evidence). The polymeric binder is also important and is assumed to contribute to adhesion of the coating to the substrate (for which some evidence exists, particularly as a mechanical linkage onto roughened, or shot-blasted, surfaces). Also intrinsic polymeric heterogeneity is thought to be important, where variation in the network crosslink density across the 3D polymer volume is assumed to increase over time (i.e. as a result of environmental stresses) eventually providing a percolating pathway for water and ionic ingress. This final concept comes out of Mayne's early studies on free films[1] and is encapsulated in the Nguyen model for coatings failure[2] which, although intellectually compelling, has limited direct supporting evidence. Thus, despite over one hundred years of research and testing, the mechanisms of coatings failure are still somewhat obscure.

2. What we know

Paint coatings are generally regarded as functioning by providing a barrier between the substrate and the environment, ideally providing a high resistance to ionic movement. Alongside these properties, it is presumed that good performance is dependent upon good adhesion, either directly or via an undercoat or primer, to the metal substrate. In order to address the relevance of these presumed mechanisms, a number of important questions must be answered. For example, can heterogeneity (defects) in paint coatings be measured and what is their influence upon coating performance? At what length scales does heterogeneity in coatings exist? What is the influence of heterogeneity in the substrate? The question of why organic coatings fail is also central. Failure may result from one or more of the following: intrinsic defects, damage accumulated in service or surface contamination under the coating. Nevertheless, coating failure frequently occurs unexpectedly in apparently intact areas. Different approaches to these questions have been followed by Mayne[1], Ngyuen[2], Funke[3], Taylor[4], Possible mechanisms advanced by these authors include: ionic and electronic resistance of the coating (Mayne and co-workers), adhesion of the coating to the substrate (Funke and co-workers), Percolating pathways leading to failure (Nguyen). The barrier effect of the coating and pigments is often regarded as self-evident, while the performance of coatings on many alloys is regarded as being driven by substrate metallurgy.

2.1 Ionic migration

According to the Mayne hypothesis, movement of ions in organic coatings is slow and rate limiting. The charge may be carried by cations or anions (or both) depending upon the nature of the polymer. Consider a clean, rust-free steel sheet coated with 25 µm of clear lacquer such as plasticised polystyrene figure 1(a). After a few weeks of exposure to the environment a red-brown deposit is observed on the surface of the lacquer and blisters containing a clear liquid may be observed underneath the lacquer figure 1(b). Charge transfer must have taken place in order for electrochemical reactions to proceed. Charge transfer is ionic in the electrolyte and electronic in the substrate, so how is charge carried in the polymer figure 1(c)? The appearance of the red-brown deposit on the surface suggests Fe^{2+} ions must migrate from the substrate into the polymer figure 1(d). The growth of the under-film blister suggests oxygen and water must migrate from the electrolyte into the polymer figure (1e).
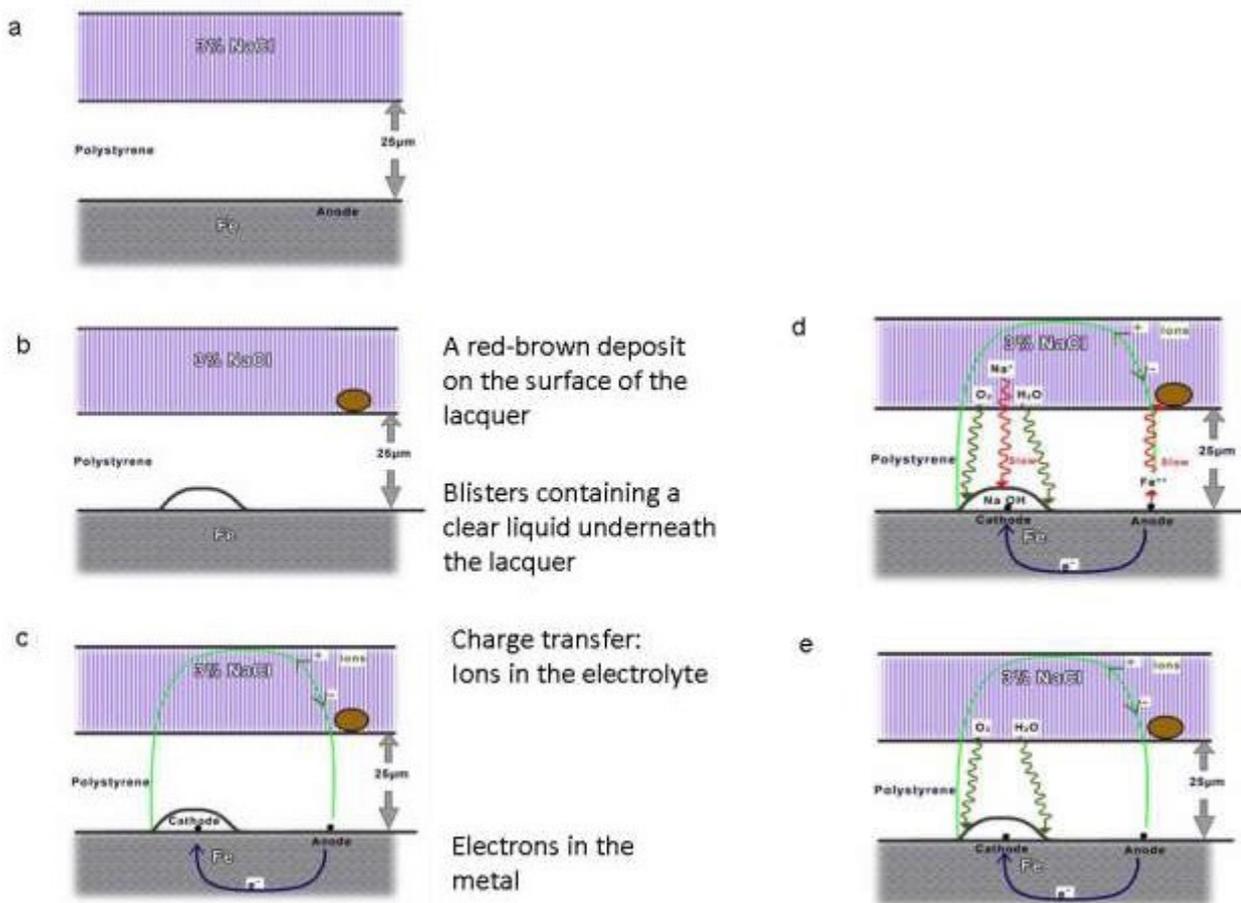

Figure 1: Experimental observations of under-film corrosion: (a) coating applied on clean substrate, (b) after a few weeks exposure to electrolyte, (c) charge transfer between electrolyte and substrate, (d) ions migrate from substrate, (e) oxygen and water migrate (images David Scantlebury).

2.2 Environmental barrier

For typical unfilled (clear) epoxy coatings, the permeation rate of oxygen is approximately 2×10^{-12} mol cm^{-2} s^{-1} and that of water is approximately 10^{-12} mol cm^{-2} s^{-1}. This is equivalent to a corrosion rate of around 10 microns per year in iron, compared with around 100 microns per year in the atmosphere[5]. Hence, restricted permeation of reactants contributes to some, but not all, of the corrosion protection observed in practice. In principle, appropriately tailored lamellar pigments can retard the movement of water and other species through coatings, figure 2. In nano-clay composite paints, polymer chains are intercalated between the initial condensed clay platelets and exfoliation leads to complete separation of the platelets to provide a highly convoluted structure. Deflorian and co-workers report up to 80% reduction in oxygen diffusion rate and 88% reduction in water diffusion rate for nano-clay composite coatings compared with unfilled epoxy[6]. However, evidence suggests that even for finely divided lamellae the reduction in diffusion rate is insufficient to affect substrate corrosion in the long term and even the best barrier will not stop corrosion arising from contamination under the coating.
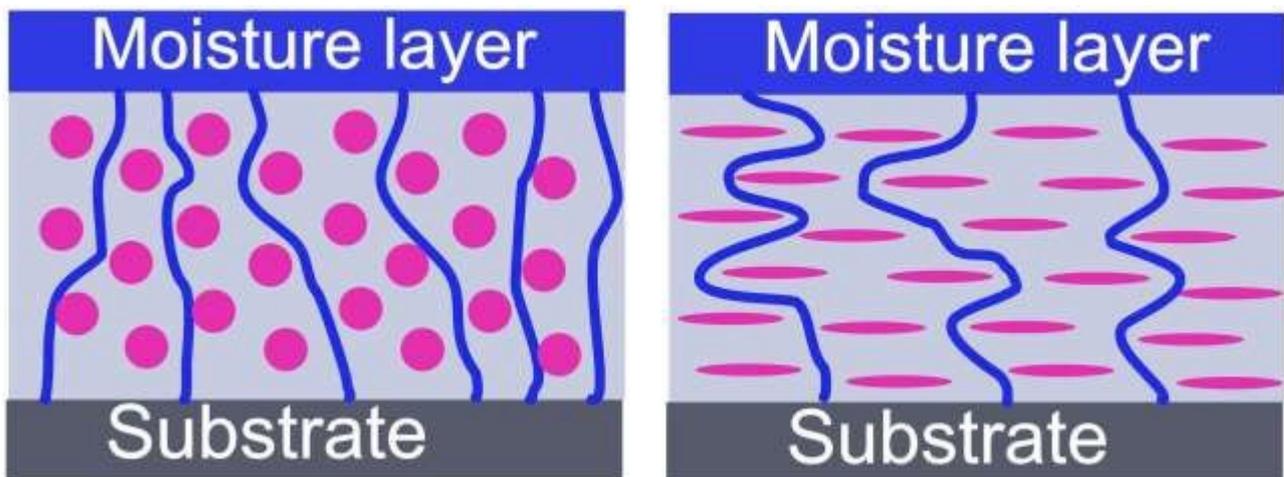

Figure 2: Barrier properties of shaped pigments: spherical pigments allow easy percolation of water while lamellar pigments create a tortuous pathway for diffusion.

2.3 Coating heterogeneity

Work by Mayne, Kinsella and Scantlebury[1,7] on detached coatings (free films) showed that cross linked systems such as penta-erythritol alkyd, phenol-formaldehyde and epoxy-polyamide showed heterogenous electrical behaviour on a centimetre length scale. Thus, on immersion in an electrolyte solution for a short time of around ten minutes, some regions of the film were found to have conductivities that were proportional to the solution (i.e. "Direct" conduction – "D" areas). Such "D" areas had relatively low resistance, typically in the range 10^6 to 10^8 Ω cm^{-2}. Conversely, in other regions of the film, the conductivity was inversely proportional to the external solution (i.e. "Inverse" conduction – "I" areas); these areas had much higher resistance (10^9 to 10^{11} Ω cm^{-2}). The films could be

defined in terms of the percentage of the film area that comprising "D" regions and the respective resistivities of the "D" and "I" regions. These were found to be reproducible parameters for a particular type of coating at a particular thickness. It was believed that water uptake into the film controlled the "I" type conduction whereas ion uptake into the film controlled "D" type conduction. More recently Jamali and Mills studied the electrical properties of coatings using the wire beam electrode at millimetre spatial resolution[8] and concluded that the majority of film area was of "I" type.

In service it is well known that the resistance of organic coatings and polymer films decreases over time due to environmental factors. This is the basis of the Nguyen hypothesis[2], which states that water uptake by the coating is non-uniform and concentrated in low molecular weight, low cross-linked hydrophilic regions (i.e. with "D" character). Environmental stress and/or exposure cause these regions to grow in size until they span the entire coating thickness, giving rise to a percolating network. This pathway then allows under-film corrosion to develop leading to blistering and associated coating failure, figure 3. This model is consistent with the delay period prior to the onset of wholesale failure on apparently intact coatings and with "bleeding" of corrosion products onto the coating surface. However, although the model is intellectually compelling, historically little direct experimental evidence has existed.
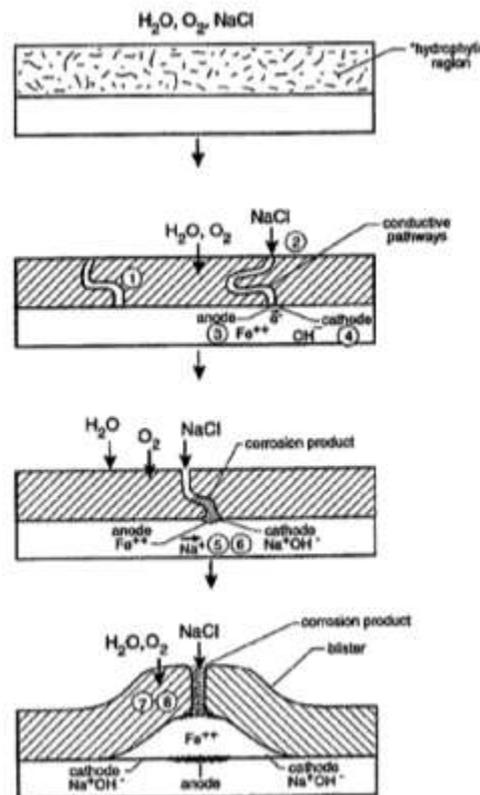

Figure 3: Schematic outline of the Nguyen hypothesis showing progressive coating damage leading to a percolating pathway through the coating and the development of under-film corrosion.

Recently, however, advances in sub-diffraction limit infra-red analysis using atomic force microscopy have permitted mid-infra chemical imaging at the nanometer scale[9]. Such work has shown that water uptake into epoxy-phenolic can coating systems is highly heterogeneous[10] and is correlated to areas unreacted epoxy that are presumed to be associated with local cross-link density and polymer network free volume. Related work has also, for the first time, confirmed a chemically and physically heterogeneous nanostructure at the same length scale within an epoxy-phenolic network[11].

2.4 Coating adhesion

In terms of the overall performance of protective organic coatings, Funke[12,13] placed great emphasis on the importance of wet adhesion to the substrate, claiming that it was a key factor in overall coating lifetime. This concept can be best summed up by the phrase "adhesion is performance". In other words the greater the (wet) adhesion strength, the better the performance. In general terms however, this idea is incompatible with the Mayne and Nguyen hypotheses where ionic migration and the development of percolating pathways would appear independently of coating adhesion. Mayne himself indicated that the absolute value of wet adhesion, beyond what was needed to keep the coating in contact with the metal, was of little importance in determining its anti-corrosion performance[14]. Similarly, Marsh et al.[15], showed that systems could be prepared that had poor adhesion with good performance (e.g. phosphated steel) and good adhesion with poor performance (e.g. silane-treated steel).

Cathodic delamination is an important degradation mechanism for coated metals exposed to the environment where adhesion might be thought to be an important factor in performance. There are two main scenarios: firstly, the delamination of intact, undamaged coatings that are subject to applied cathodic protection; secondly, disbonding of coatings ahead of a through-thickness coating defect. The presence of alkali metal cations is generally essential for failure to occur and it is also accepted that either interfacial alkalisation[16], or the formation of free radical intermediaries during the step-wise reduction of oxygen[17], are responsible for coating failure. A correlation of disbonding rate with cation mobility or diffusivity for coatings under cathodic protection was first noted by Leidheiser[18] who found, for model polybutadiene coatings, that ionic diffusion through the film thickness accounted for the observed disbonding kinetics. A similar finding was confirmed by Skar and Steinsmo[19] and this makes sense because cathodic substrate polarisation encourages electromigration of cations through the coating to the substrate. However, for defects that arise as a result of service damage (i.e. a scratch)[20], or for thick coatings[21], although oxygen ingress through the coating thickness is still necessary, it is generally accepted that it is the kinetics of ionic diffusion along the coating-metal interface that controls the overall rate of disbonding.

As an example, to determine whether coating adhesion influences the cathodic disbonding rate, silane adhesion promoters were used on steel to modify the interfacial coating-substrate chemistry[22]. Application of an epoxy coating to a substrate pre-treated with 3-glycidoxy propyl silane resulted in both increased wet adhesion and improved resistance to cathodic disbonding. Similarly application of an alkyd coating to a substrate pre-treated with 3-amino propyl silane also caused an increase in wet adhesion. However, and importantly, no such improvement to the cathodic disbonding resistance was observed. These observations demonstrate that physical adhesion has no intrinsic effect on cathodic disbonding resistance. So it appears that cathodic disbonding is a chemical effect and can be controlled by interface and binder chemistry and that coating adhesion is a necessary, but not sufficient, condition for good coating performance.

2.5 Metallurgical heterogeneity

The majority of engineering alloys contain metallurgical additions that form a strengthening phase (e.g. carbide particles in low alloy steel and intermetallic precipitates in light alloys). In many cases, but particularly for light alloys, the electrochemistry of the 2nd phase particles is substantially different from the parent metal, Table 1.

Phase	Corrosion potential (mV v. saturated calomel electrode)		
	0.1M NaCl; pH 2.5	0.1M NaCl; pH 6	0.1M NaCl; pH 12.5
Al_3Fe	-510	-566	-230
Al_7Cu_2Fe	-535	-551	-594
Al_2Cu	-546	-665	-743
Al matrix		-750	
Al_2CuMg	-750	-883	-670
$MgZn_2$	-1007	-1029	-1012
Mg_2Si	-1408	-1538	-1553

Table 1: Corrosion potentials for selected 2nd phase particles that are common in light alloys[23,24]

Thus, such particles can be either strong net local anodes or cathodes[25]. In addition, the condition of the material can vary significantly with depth. For example, the number density of 2nd phase particles in the aerospace aluminium alloy AA2024-T3 typically doubles[26] from the bulk (~5 x 10^5 cm^{-2}) to the surface (~11 x 10^5 cm^{-2}) while the average particle size drops by around 3 times (from ~7 μm to ~ 2 μm) for an overall surface area fraction of 2.8%. Consequently, the presence of such phases in the substrate surface

drives damage processes in the organic coating; at local anodes corrosion gives rise to anodic undermining of the coating while at local cathodes coating failure occurs via cathodic delamination.

2.6 Surface preparation and inhibition

Apart from a limited number of important but niche applications (e.g. internal coatings for food and beverage cans) organic coatings cannot provide reliable corrosion protection alone.

3. What we'd like to know

The remaining part of this paper looks at areas where further work could be usefully conducted This includes study of the oxide or hydroxide film under a coating , the effect of surface preparation, oxygen and water permeability, ionic conduction and film inhomogeneity, adhesion and cathodic disbondment, and inhibitors.

3.1 The Oxide or Hydroxide Film?

The criticality of the oxide or hydroxide film on the substrate beneath the coating needs to be addressed. Does this layer grow? Does passivation occur (i.e does the oxide layer develop into a uniform barrier) e.g. under an I type film when exposed to solution). There is some evidence that a barrier to aggressive ions does form when the potential is high, as this leads to a high level of oxygen diffusion and some water diffusion through the coating, hence favouring oxide/hydroxide layer growth. **(**Brook and Pearson paper **(ref DJM needs to find reference)** A useful experiment would be to take a highly polished piece of iron, coat it uniformly with varnish (I type) e.g. paralyne, or with a transparent electrocoat. Expose the coated specimen to solution and attempt to monitor oxide growth using ellipsometry. After the exposure test, the coating could be stripped and the surface composition examined (e.g. by x-ray diffraction). It would also be interesting to see whether the oxide layer from previously exposed coated steel from which the coating has bene stripped takes longer to break down.

3.2 Surface preparation

It would also be useful to do further work to confirm the criticality of surface preparation and explain it. For example, if water jetting is just as effective (if not more effective) than, say, grit blasting, we need to know why.. The evidence to-date suggests that water jetting is the best method, but work is needed to confirm this and to understand why. The homogeneity of the oxide film appears to be critical

3.3 Water and Oxygen Permeability?

As discussed earlier in this paper oxygen and water permeability play a part although less critical than There have been water and oxygen permeability studies [27,28] but further investigation is needed to determine the permeability criteria. The hypothesis is that permeability of both species is desirable (mainly for growth and maintenance of a oxide film), But too high a level of permeability is deleterious.

3.4 Ionic Conduction and Inhomogeneity

It remains generally accepted that a key role for a coating is to act as a barrier to ions. The concept of D and I areas was introduced earlier in the paper A full 3D model of inhomogeneity in organic coatings system needs to be developed. An example of a 2D model has been given recently with the system envisaged as is an I type continuum with small D regions distributed within it. (This would be analogous to a metal substrate with second phase particles which vary apparently randomly in distribution and also in size). The figure below shows an example
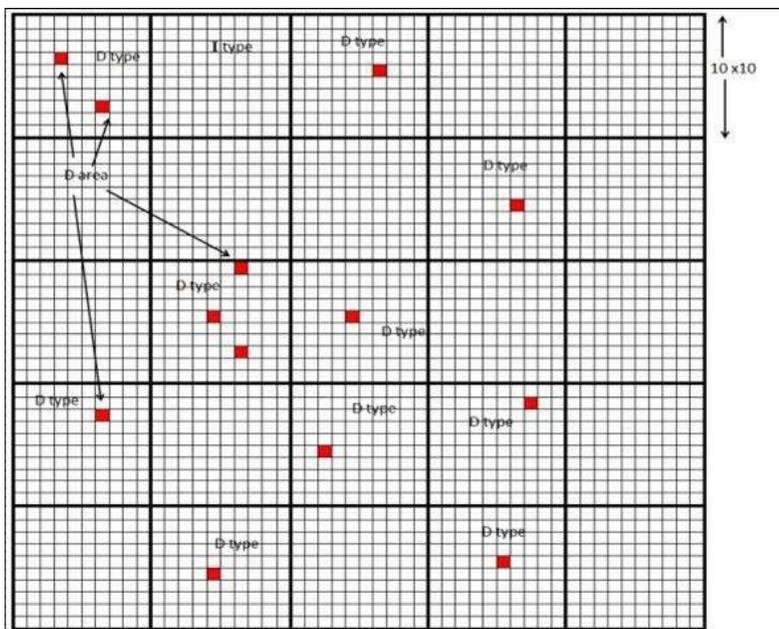
Figure 4: Mathematically created model of D area distribution for 40% D type film (total of 13 D areas) assuming Poisson distribution (reproduced from reference 12)

Note that inhomogeneity may arise as a inevitable consequence of the film forming process – this could be expressed mathematically eg using something similar to Alan Turing's theory of Morphogenesis The latter explains how significantly different local chemical concentrations can arise at different points from an originally totally homogeneous starting condition. Theoretical work could be done to see if this theory mutandis mutatis has applicability to the forming of solid networks of polymer. One important

questions is can a 100% I type film be achieved? There is at least one coating system, specifically an electrocoat, where no D type areas have been seen. At 25 - 30 μm a good quality electrocoat presents an homogenous, highly effective, barrier to ions. **[ref** Mills, Berg and Bierwagen **ref** DJM needs to locate this Proceedings of ACPOC **1994]** Techniques such as AFM can be used to pick up physical differences which could be located on a grid. Complementary methods such as ESCA (Electron Spectroscopy for Chemical Analysis) and Fourier Transform Infrared spectrometry (FTIR) might then be used to look for chemical differences. A method of highlighting D type areas would be useful, e.g. a technique that will pick up only through D type films. Surface D regions could be of interest, but only if their thickness relative to the thickness of the film. Is know

3.5 Adhesion and cathodic disbondment

Apart from further work looking at the effect of the adhesion and interfacial chemistry, confirmation is needed that the rate of cathodic disbondment is frequently controlled by ionic conduction through the coating . Future investigations may aim towards testing the postulate that to get low rates of cathodic disbondment both with and without a defect and with and without applied potential a high ionic resistance is needed . This means a 100% I type film; any D areas present in the vicinity of a defect will be likely to be detrimental and will increase the rate of disbondment

3.6 Inhibition

4. Concluding remarks

This brief over review has attempted to show the state of knowledge at the present time about how paint coatings work to prevent corrosion . There are still a number of unanswered questions Hence there is plenty of interesting scientific work still to do before we can claim to really understand this subject . Hopefully this paper will help to allow more pieces of the jigsaw to be filled in!

5. References

[1] E.M. Kinsella, J.E.O. Mayne, Br. Polym. J., Vol. 1, pp.173-176 (1969)

[2] T. Nguyen, J.B. Hubbard, J.M. Pommersheim, J. Coatings Technol., Vol.68, pp.45-56 (1996)

[3] W. Funke, in: "Polymeric Materials for Corrosion Control", eds. R.A. Dicke, F.L. Floyd, ACS Symposium Series, Vol. 322, pp.222-228 (1985)

[4] S.R. Taylor, IEEE Transactions on Electrical Insulation 24, No. 5, 787-806 (1989)

[5] S.B. Lyon in "Shreirs' Corrosion", 4th edition, ed. J.R. Richardson, Vol.3, pp. 1693-1736 (2009)

[6] S. Kenig, F. Deflorian, R. Cafagna, Proceedings 30th FATIPEC conference, Genoa, Italy (2010)

[7] J.E.O. Mayne and J.D. Scantlebury, Br. Polym. J., Vol. 2, pp. 240-243 (1970)

[8] S.S. Jamali, D.J. Mills, Corr. Eng. Sci. Tech., Vol. 48, pp. 489-495 (2013)

[9] K. Kjoller, J.R. Felts, D. Cook, C.B. Prater, W.P. King, Nanotechnology, Vol. 21, 185705 (2010)

[10] S. Morsch, S.B. Lyon, P. Greensmith, S.D. Smith, S.R. Gibbon, Faraday Discussions, Vol. 180, pp. 527-542 (2015)

[11] S. Morsch, Y. Liu, S.B. Lyon, S.R. Gibbon, Applied Materials and Interfaces, Vol. 8, pp.959-966 (2016)

[12] W. Funke, J. Oil and Col. Chemists Assoc., Vol. 62, p.63 (1979)

[13] W. Funke, H. Leidheiser Jr., J. Oil and Col. Chemists Assoc., Vol. 70, p.121 (1987)

[14] J.E.O. Mayne, private communication

[15] J. Marsh, J.D. Scantlebury, S.B. Lyon, Corros. Sci, Vol. 43, pp.829-852 (2001)

[16] H. Leidheiser Jr., W. Wang, L. Igetoft, Prog. Org. Coat., Vol. 11, pp.19-40 (1983)

[17] P.A. Sørensen, C.E. Weinell, K. Dam-Johansen, S. Kiil, J. Coat. Technol. Res., Vol. 7, pp.773-786 (2010)

[18] H. Leidheiser Jr., J. Adhesion Sci. Technol., Vol. 1, pp. 79-98 (1987)

[19] J.I. Skar, U. Steinsmo, Corros. Sci., Vol. 35, pp.1385-1389 (1993)

[20] A. Leng, H. Streckel, K. Hofmann, M. Stratmann, Corros. Sci., Vol. 41, pp.599-620 (1998)

[21] P.A. Sørensen, K. Dam-Johansen, C.E. Weinell, S. Kiil, Prog. Org. Coat., Vol. 68, pp. 283-292 (2010)

[22] MK Harun, J Marsh, SB Lyon, Prog. Org. Coat., Vol. 54, pp.317-321 (2005)

[23] N. Birbilis, R.G. Buchheit, J. Electrochem. Soc, Vol. 152: B140-B151 (2005)

[24] N. Birbilis, R.G. Buchheit, J. Electrochem. Soc., Vol. 155: C117-C126 (2008)

[25] A.E. Hughes, N. Birbilis, J.M.C. Mol, S.J. Garcia, X. Zhou, G.E. Thompson, in: "Recent Trends in Processing and Degradation of Aluminium Alloys, ed. Z. Ahmad, ISBN: 978-953-307-734-5, pub. InTech (2011)

[26] A.E. Hughes, A. Boag, et al, Proceedings of "Aluminium Surface Science and Technology", Beaune, France, ATB Metallurgie, 45 (1-4): 551-556 (2006)

[27] N.L. Thomas, J. Corros. Sci. Eng. 8, preprint 11 (2004)

[28] S. Jamali, P. Mokhtarian, D.J. Mills, Prog. Org. Coat., Vol. 87, pp. 20–27 (2005)