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The best tests for Anti-Corrosive paints. And why: a personal viewpoint.

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Abstract

This paper starts by putting forward a mechanism for the way that anti-corrosive paints work. This draws on previous work on understanding of mechanism but puts stronger emphasis on the maintenance of the oxide film of the metal under the paint as the essential feature. If this mechanism is correct then it suggests various properties which a paint coating should have. In many cases a minimum value of these properties is all that is required. In some cases eg DC resistance, it is advantageous to have as high as possible value of this property at the start due to degradation with time. The paper then details a series of tests, chosen by the authors for their relative simplicity, to measure these properties in a quantitative manner and hence to assist in formulation of new or better coatings. These tests are the personal selection of the authors and we admit that others may make different choices. They have been divided into those best conducted on the free paint film and those which are conducted on the metal and paint together, the latter including one test to be conducted on the metal alone. Among the second group, suggestions have been made for electrochemical tests which are non-destructive and can thus be used for quality control and monitoring. There is a brief discussion of accelerated tests with the emphasis again on quantitative non-destructive assessment methods. Numerous pertinent references are provided. The paper concludes with suggestions for future work.

Introduction

The purpose of the paper is to suggest the best tests to assess candidate paint materials both in the laboratory and in the field. There is a brief review of mechanisms and then a personal selection by the authors based on a lifetimes' experience. One of the authors has attempted to do this before [1]. But that was eleven years ago. And it is time for an update. Firstly let us define what we mean by a paint. It is not necessarily the same as a protective polymer coating. The definition we are working on is that a paint is something that is a relatively simple mix of binder/solvent/ pigments. It can be applied easily e.g. by spray. It normally dries by loss of organic solvent and this may or may not be followed by chemical cross-linking reactions. Sometimes what is known as a paint might exclude solvent, e.g. UV curable systems, or contain water in place of organic solvent to reduce viscosity and be more environmentally friendly. Paints in general are a relatively cheap way of protecting metal. Applicators would prefer single pack but they can live with double pack. Zinc rich epoxy only just makes this definition. However having defined a paint, it is necessary to ask why we have emphasised certain tests and not others? Well, to support our choice, in the first part of the paper, we have suggested a mechanism by which anti-corrosive paints work and provided some justification for this mechanism (another paper in this volume looks at mechanism in more detail [2]). Ionic resistance is highlighted as an important (even critical) property of coating. This can be measured both when the coating is detached (free film) from the metal substrate and when it is attached (in-situ). In the latter case the value measured may have a component that is something other than the ionic resistance of the coating. But it is the authors' contention that generally (certainly for coatings that are operating successfully with resistance greater than $1E6 \text{ ohms-cm}^2$) the dominating resistance is the ionic resistance. This stress on the importance of resistance is based on a large amount of experimental work done over several decades both on detached films [3–7] and on attached films [8–11]. But most of these experiments were quite short term. The long-term experimental work done using in-situ DC resistance was done nearly seventy years ago [12] and has not, to the authors knowledge, been repeated since. So, to justify our emphasis on DC resistance (or its equivalent measurement i.e. R_n from electrochemical noise measurement (ENM) or 0.1Hz Impedance from EIS measurements) as a very important property, some recent results have been obtained on the long-term resistance behaviour of one particular coating. This leads to our suggestions as to the best tests (i.e. the tests we think are best based on current knowledge) which should be made on detached coatings and the best tests on attached coatings. This review ends with a section on future work in relation to improving or buttressing these test methods.

Mechanism

How do paints work to prevent corrosion? The early “barrier to water and oxygen” theory was disputed by Mayne [13] in 1952, who showed that coatings were permeable enough to oxygen and

water to support corrosion at the rate it would have occurred if the coating had not been there. So the way a paint protected had to be due to something else e.g. acting as a barrier to ions. The standard Mayne explanation is that the paint provides a high resistance between anodes and cathodes. This slows the rate of attack down to negligible. However, although agreeing in principle with Mayne's contention the authors would like to bring to the fore a corollary to this and suggest that a very important function of a paint coating is to maintain the oxide film under the coating in the best possible condition i.e. to aid passivation:



One needs to avoid a situation where the oxide might be reduced, e.g. acidic conditions where the cathodic reaction can become:



Hence (and here we are putting emphasis on something that has not hitherto been stressed very strongly) one needs to encourage oxidizing conditions at the paint/metal interface. Success in achieving this is often manifested by the coating system (i.e. coating/metal substrate combination) presenting a high, in-situ, value of DC resistance. As well as imposing a high resistance between anode and cathode, this high resistance barriers out aggressive ions (note that resistance of the detached organic coating will be related to, although not necessarily the same as, the in-situ resistance). The authors admit that more evidence needs to be gathered to "prove" the "oxide film maintenance" theory. We put it forward as, as good an explanation as any for some of the results obtained from working (a combined) sixty years on and off in anti-corrosive paints research where other theories fail. So what justification is there? The standard (Mayne) explanation is that the corrosion rate is controlled by whatever the value of resistance is between anodes and cathodes. But this "gradation" theory may not be the whole story. When Brook et al [14] considered the Pourbaix diagram for iron and then combined that with kinetics, they found that when ionic resistance reaches a certain value (around 10^7 ohms), then passivation will "set in" as long as there is a passivating species in the environment. It is, of course, generally noted (as it is with bare metals) that high potentials (e.g. -0.2V SCE or above) for coated metal are associated with a paint coating being effective at protecting. And that when the paint breaks down the potential normally falls [15]. Scantlebury and Faidi [16,17] did some interesting work in high resistivity organic liquids which confirmed this.

So it is our contention that to create conditions for achieving growth and maintenance of a "good" oxide at the metal-oxide interface below the paint is a very important aspect for what the paint needs to do. Hence it needs to prevent aggressive species, e.g. chloride ions, from penetrating. It should prevent acidity accumulating at the paint-metal oxide interface. And also it should not have

components within it which are aggressive to the metal. At the same time it needs to encourage (well at least not discourage) passivating species at the interface, e.g. water (water can be an oxidizing agent) and oxygen [18]. This would suggest a certain minimum level of oxygen permeability is to be encouraged. Note although oxygen permeability does NOT control corrosion rate when a paint is protecting, it may do so later in the life of the coating when the paint resistance is so low it is no longer protecting [19]. Another factor, which becomes particularly important when the resistance property of the paint has broken down, is that the primer coat should make available inhibitive ions at the paint/metal interface. A third factor is that, to aid stable oxide formation, the surface of the metal needs to be free of ionogenic impurities prior to application of the coating, unless the coating contains compounds which will “tie up” these species (for example, surface tolerant coatings like red lead in linseed oil). Also, the coating needs an adequate level of wet adhesion. Without this it will not function properly. Maintenance of this “good oxide” is normally associated, assuming the coating is adhering to the metal, by the system (solution, coating on metal, metal-coating interface) exhibiting a high through-film DC resistance. (However the reverse ie high DC through film resistance means protective may not “work” 100% of the time- see later). In relation to this, work conducted studying ionic conduction in coatings [3–7] found that paint coatings are inhomogeneous in their resistance behaviour, particularly thermoset type coatings. There are areas of relatively easy conduction labelled as D areas. However these probably only occupy a small fraction of film (e.g. <1%). Note that the conduction in these areas is still much slower than if they were pores filled with the external solution. D areas are innate in cross linking polymer coatings and are most often found if a single coat is applied at a thickness of anywhere between 20 μ m and 100 μ m. Double coats show much less chance of D areas than single coat at the same thickness [20]. With a triple coat film there is almost no chance of overlapping D areas so the film becomes I type, i.e. it exhibits a uniform high value of resistance. However even if the whole coating area is almost impermeable to ions (ie initially all I type), D areas may form with time (due to “impacts”). Therefore any test programme for anti-corrosive coatings should incorporate measurements to investigate the stability of resistance over time.

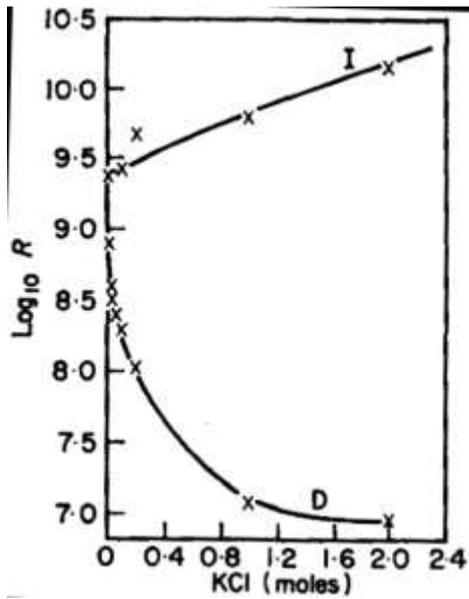


Figure 1 Variation of resistance with concentration of KCL solution for I and D type paint coatings [6].

Confirmation of importance of In-situ “Ionic” Resistance measurement

As mentioned above the classic work by Bacon, Smith and Rugg in 1948 [9], put the emphasis on in-situ DC resistance as an important property. In that work the DC resistance of 300 paint specimens were measured and the values correlated directly with protection afforded: good protection was associated with maintaining a resistance of $>1E8$ ohms-cm², fair protection (started high but fell) was $1E6$ - $1E8$ ohms-cm² and poor (started quite low and fell) was $<$ than $1E6$ ohms-cm².

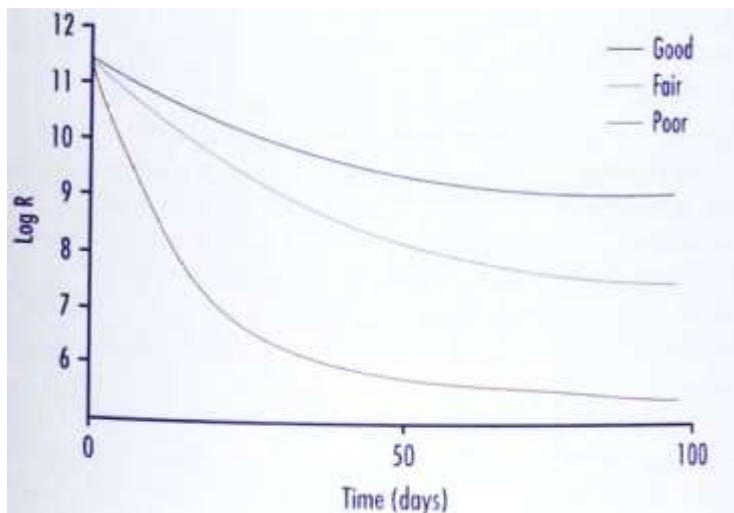


Figure 2 Schematic of resistance results obtained by Bacon Smith and Rugg for good, fair and poor coatings.

Although the present paper is not an experimental paper, because this classic work was done so long ago (in 1948) it was felt necessary to repeat it on a modern system to bolster the arguments as to which the best tests should be. The conditions were a waterjet blasted low carbon steel surface, single coat alkyd coated sample, reasonably thick 80-100 μm , sprayed on, with homogeneous thickness. Fifteen 3.14 cm^2 areas were immersed in 3% NaCl for three years (the 3% NaCl was replenished about every three months). The DC resistance was monitored during this period for each individual sample (see later in this paper for some details on the method). Results (previously unpublished) of these fifteen samples are shown in figures 3 and 4.

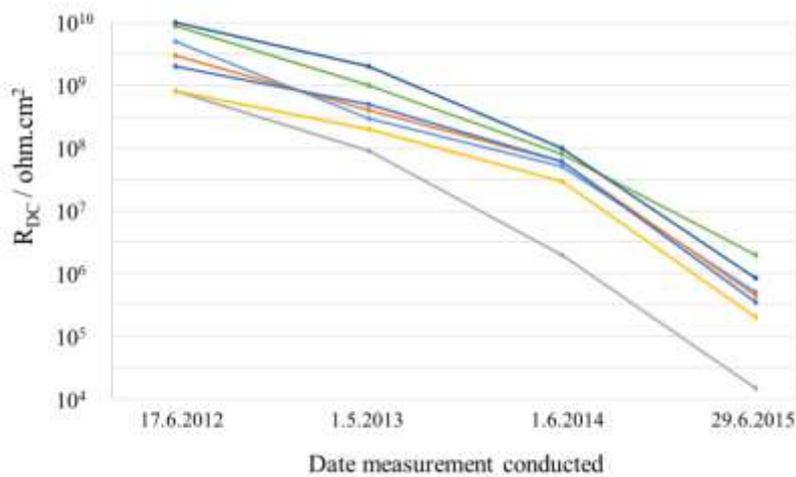


Figure 3 Seven specimens with 3.14 cm^2 area, alkyd coating –resistance followed over three years in 3% NaCl.

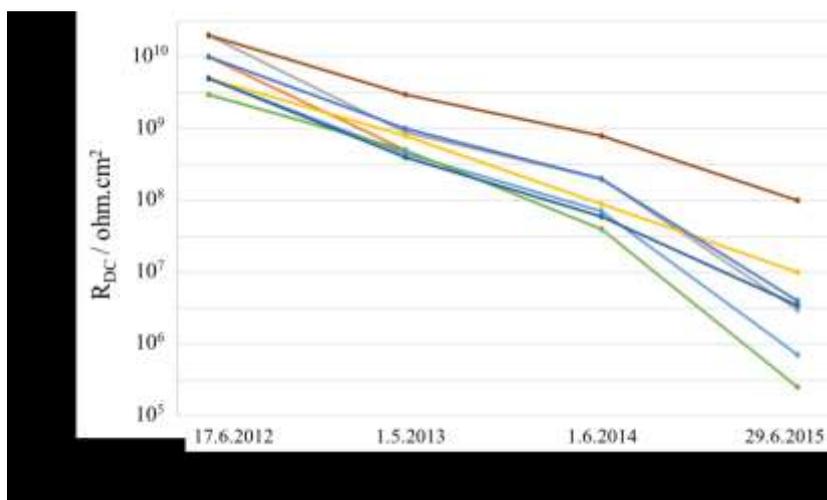


Figure 4 Further eight specimens with 3.14 cm^2 areas, alkyd coating –resistance followed over three years in 3% NaCl.

This alkyd coating is not a highly protective paint. It is formulated for use as a single layer maintenance coating in not too aggressive atmospheres maybe C3. Yet as shown in figures 3 and 4, for over two years the resistance of 14/15 areas remained high (i.e. above 10^8 ohms.cm²) and there was no corrosion. However, there was steady drop in resistance over that period which accelerated between year 2 and year 3. Note that the scale of resistance value is logarithmic and acceleration in drop of resistance refers to comparing each point to the previous measured value rather than the original resistance. One area dropped below the 10^7 ohms.cm² value after two years and that area subsequently showed corrosion. Towards the end of the test, the resistance of all the other areas started to drop and after a few further months, general rusting and blistering could be seen on the samples.

This long term test unleashed the surprising fact that over three years in immersion in a quite aggressive environment (3% NaCl at 20 +/-5 °C and about 12 concentration cycles of 20-30% due to evaporation), this “standard” single coat paint at around 80 µm thickness provided a remarkably high level of protection to the carbon steel substrate. One explanation for why it performed so well is that although there were initially some D type areas in the coating, the waterjetted substrate encouraged good oxide formation and what small amount of chloride penetrated was unable to break this oxide down. This, coupled with high adhesion and formation of inhibitive compounds [21], was sufficient to prevent breakdown and maintain high resistance. The second explanation is that there were no D types in the 15 areas chosen. This is possible but statistically unlikely based on the work done on this alkyd when detached [5]. Also previous work on alkyd coatings [20] found that, at 80-90 µm thickness, there were a significant number of D types.

However, despite its good overall protection, it seems that over long periods of time this alkyd-soya oil coating does break down, allow ionic transport and eventual failure. And this behaviour can be “picked up” by DC measurement. In practical situations this could be due to impacts from UV light, salt and free radicals as well as physical damage. A degradation process which could affect resistance would be “oxidation” of the coating’s surface such that, gradually, hydrophilic regions form allowing more water to enter and D type conduction to ensue. There might also be an ion-exchange process within the coating, identified some years ago, and called a *slow change* [7]. It was shown in that early work that the slow change (taking place over months or years) leads to exactly the same changes (ion exchange processes within the film) that take place over a much shorter time at 65°C, i.e. raising the temperature accelerates the actual mechanism that is leading to the reduction of resistance of the coatings over a longer period of time. In some cases I types were actually changed to D Types. Also, the above work [7] looked at the effect of acidic conditions (not normally deleterious to the coating at

least with regards to this mechanism), alkaline (quite often deleterious) and strength of chloride solution. Variation in the latter can change I types to D types (reversibly) as shown in Figure 5.

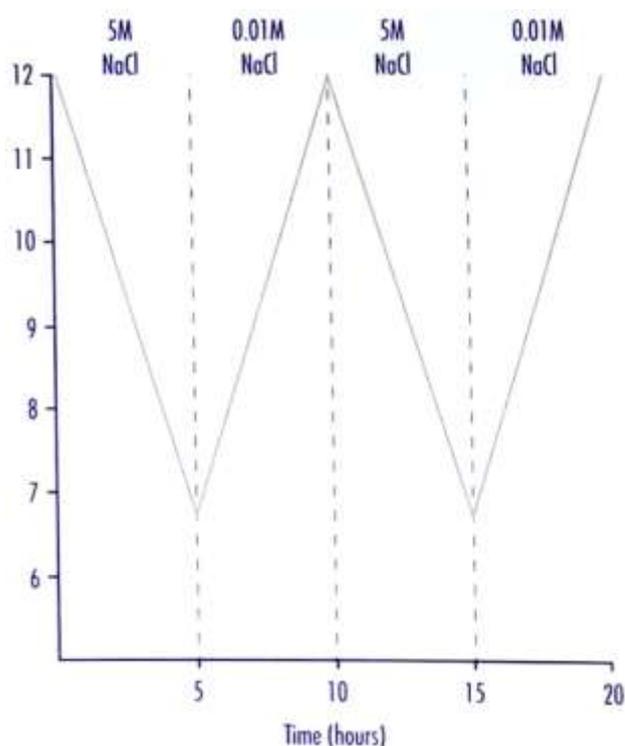


Figure 5 Effect of high temperature conditioning on resistance of paint measured at room temperature in different chloride solutions.

The above small amount of experimental work and the prior and subsequent discussion of mechanism (admittedly in some cases speculative) provide our justification for the choice of tests that follow.

Laboratory tests: introduction

It is indisputable that analysis and imaging techniques like AFM, ESCA, NMR, SVET, ellipsometry, FTIR, GDOS and SKP can be utilized to assist in investigations into anti-corrosive paints. There are many examples of their use within the papers in this special ACPOC volume. These undoubtedly have a part to play in helping us make paint more protective for longer e.g. sophisticated analytical and structural investigation methods can show what changes are brought about as results of ageing (impacts) and hence assist in the design of paints that will resist these impacts. However, most companies, whether producers of paint or users, do not have access to this gamut of methods. So, as we have in mind in making this selection the small paint company, and also to a lesser degree the

specifier and user of anti-corrosive paint, we are not going to give details on these methods and their possible applications in this review.

Laboratory tests: free film

Permeability tests (oxygen, water and ions)

Firstly let us consider measurement of oxygen permeability. This is done by having a controlled oxygen supply on one side and an oxygen sensor on the other e.g. a platinum electrode (see Figure 4). Note that interesting work by Bilder et al (1987) [22] indicated that water and oxygen compete for diffusion pathways (oxygen permeability is less from high water activity solutions and higher from low water activity solutions). Secondly water permeability can be measured by the Payne cup method [23]. Also, water uptake can be simply measured gravimetrically [24]. Both of these are standard methods. Additionally there is an electrochemical method (AC impedance/EIS) originally suggested by Brasher and Kingsbury which enables water uptake to be assessed by measuring the capacitance component of the impedance of the coating [25].

Thirdly, and most importantly, the ionic conductivity of film should be measured. Note because of the inhomogeneous nature of organic coatings particularly cross-linking types, in relation to their electrochemical behaviour, this has to be done on a number of small samples (preferably twenty- area might be between 1 and 4cm²). The standard approach is to mount samples of the coating in small U bend cells and measure DC resistance using a high impedance electrometer. Area, solution, temperature are all factors that can be varied (see figure 6a). A method has been suggested recently for quick measurement [21] using circular pieces of coating on a stainless steel base with a drop of solution on one side and a thin aqueous layer on the other (see figure 6b). As mentioned above, it is important to know the exact thickness of every piece of coating that is measured. Duration of exposure is also an important factor so the resistance versus time (a time line) can be established.

Regarding tests to accelerate the reduction in ionic resistance, this is best done by making DC resistance measurements on the detached film in the most likely environment as a function of time. There is likely to be criticism of doing this only on detached films by those who consider that the main cause of the reduction in a coating's resistance is from the creation of aggressive (to the coating) products from reactions at the steel-coating interface [26]. The authors do not deny that this is possible. So, in order to simulate performance of the coating under conditions where different chemical conditions may start to occur, it is recommended that measurements (still on detached films) are made in dilute acid (pH4) , in dilute alkali (pH 11.5 or 12) and in ferric chloride solution. Note that the temperature can be raised to accelerate the degradation process e.g. to 65°C.

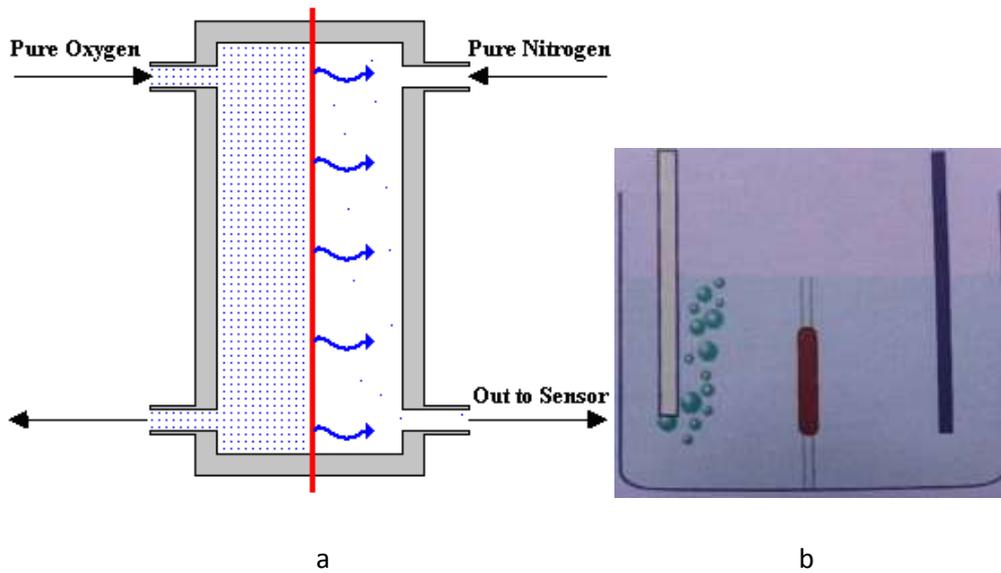


Figure 6 Schematic representation of measurement set-up for oxygen permeability a) dry b) wet

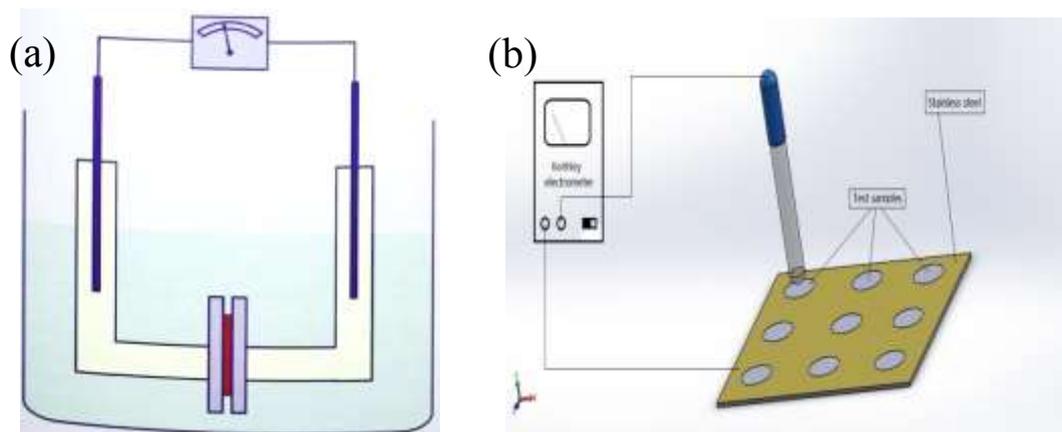


Figure 7 DC resistance measurement: a) standard b) quick test using an electrometer

Corrosion Inhibition tests

If there are soluble chemicals in the coating, these may be leached out when water penetrates the coating and affect the corrosion rate at the interface. Inhibitive anti corrosive pigments are a popular addition to primers. But corrosion tests performed on the aqueous extract from the pigment are of limited use. This is because the environment inside the paint is very different to the one when the pigment is free to interact directly with water. Far better are corrosion tests conducted on the leachate from the coating. This involves extracting what is present in the coating, normally conducted at elevated temperature e.g. 50°C by putting pieces of detached coating in contact with distilled water (see figure 8). Subsequently pieces of clean weighed steel are placed into this extract (see figure 9),

left for a week or a month in a controlled temperature and humidity environment and then reweighed. This enables the corrosion rate to be calculated. There are four possible results: no change from blank/control solution, total inhibition, acceleration and partial inhibition. The tolerance of the inhibitor to aggressive ions can also be investigated in this simple test. Such tests can show if soluble chemicals in the paint (e.g. certain pigments) are corrosive or whether they act as restrainers. In the best cases the extract from the coating will lead to total inhibition (e.g. red lead in linseed oil-alkyd and zinc or strontium chromate (VI) in just about any binder –Benchmark test). Note in the case that they are corrosive (and particularly when they get trapped under the coating, a high in situ resistance measurement may give false indication of the protection (similar to as if the surface had been contaminated before the paint was applied). So this is an important test.

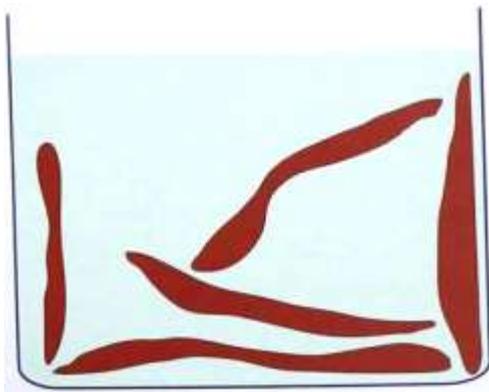


Figure 8 Leaching test on detached pieces of coating



Figure 9 Small beaker (pot) test to estimate corrodibility of substrate and corrosion/inhibition in extracts from paint.

Glass transition temperature (T_g) characterisation

On detached coatings a dynamical thermal analysis (DTA) or dynamical mechanical thermal analysis (DMTA) measurement can be made. The Glass transition temperature (T_g) needs to be known both with the film dry and wet [27]. The latter can be estimated from the way the resistance varies with temperature [28]. I type resistance, in particular, is strongly influenced by transitions in the polymer [5,29]. Apart from influencing water uptake and ionic resistance, the T_g will also have an impact on leaching rate of inhibitive (or aggressive) species from the coating.

Laboratory tests in-situ for coating on metal

Electrochemical testing

Regarding the metal substrate in general this discussion below has plain carbon steel (C concentration from 0.015 to 1.5% in any heat treatment condition) in mind. Following on from Bacon, Smith and Rugg [12] and the experimental work described earlier, it is recommended that the resistance (at 0.1 Hz if using EIS .Note other frequencies are NOT comparable [30]) is measured as a function of time. Note this is normally done on a specific area e.g. defined by a cell in leak proof contact with the coating (see figure 10). Apart from DC resistance (which has advantages of being very simple to conduct) other methods such as EIS, ENM as well as C.I. (Current Interrupter technique) can be used to obtain the R values that are proven to be close to R_{0.1 Hz} [31,32]. Note that if the paint film is protecting the metal substrate effectively, the “R” is normally dominated by the ionic resistance of coating. If the paint has broken down the “R” may have a significant “interface (metal/solution)” component. It is believed, however, that, regardless of what makes up this resistance, the R value is still the most easily measured parameter which will give a quick assessment of the coating’s protectiveness.

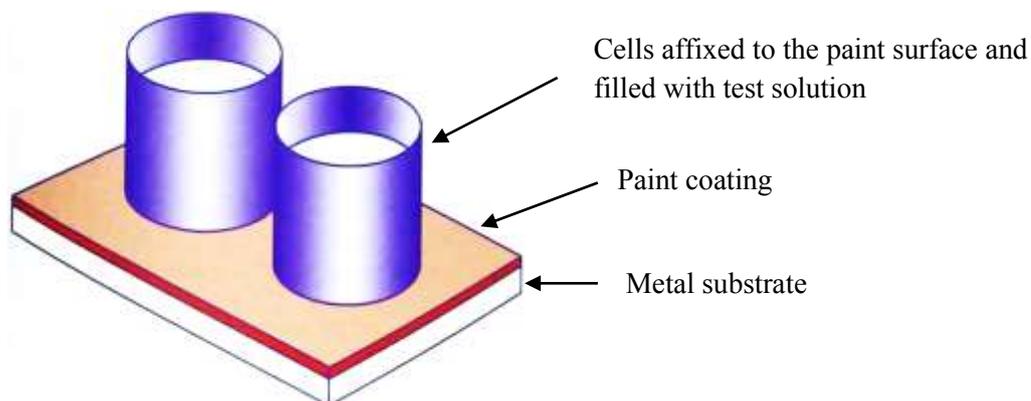


Figure 10 Schematic of method for electrochemical testing of coated metal in contact with solution using affixed tubes to the surface of paint.

Note that in-situ DC resistance measurement can also be used to test for the effectiveness of inhibitors (assessment at cut edge/scribe [33]) although the values for good, fair and poor protection are two or more orders of magnitude lower than the Bacon, Smith and Rugg criteria. The authors would also use EIS here (maybe ENM also) as in this situation the corrosion reactions are dominating. Note that galvanostatic EIS is preferred over potentiostatic. This is because, similar to DC resistance measurement using a high input impedance electrometer such as Keithley electrometers, the minimum external current required to get a measurable reading is applied [34]. Although potentiostatic EIS is more popular, it applies a constant potential perturbation which because of the variable impedance at different frequencies causes variable current to be applied across the electrodes. This might affect the accuracy of measurement.

For very high resistance coatings (which can be virtually unmeasurable at 20°C), it is recommended that the temperature is raised to 65°C. If a measurable result can still not be obtained, the temperature can be further increased to 75°C. Based on typical values of activation energy, conduction processes will go on about 50 times faster at 75°C than at 20°C. This makes resistance more easily measurable and any degradation processes (see discussion of slow change above) will be significantly accelerated, e.g. one year is one week. Note although the T_g may be exceeded, these sort of temperatures, although they may only occur occasionally, are not unrealistic for many coatings used in atmospheric environments.

It is very important to know the thickness value of coating when measuring ionic resistance. This is because of the remarkable impact of thickness on this parameter, e.g. a doubling of thickness might lead to a many orders of magnitude change in the resistance. So, for all areas/pieces of coating used for any of these tests, the thickness of coating must be known. And, where a large area is used in the test, the average thickness and standard deviation should be measured. It is also very important to know how homogeneous the resistance value is. In work reported previously [1] there is discussion on how this can be assessed by measuring a large area and comparing the value with the expected value based on the measurement of say 10 small areas within the large area.

Adhesion

Adhesion is important. But, in the authors' view, in most general situations the value only has to be above a certain critical value. The absolute value is more critical in relation to cathodic disbondment and with cut edge corrosion where the rate of disbondment can be affected by the adhesion. Note that permeability factors can also play a part and influence adhesion. For example, there is evidence that

disbondment (under cathodic protection or CP conditions) is often controlled by ion transport through the coating [35–37]. Regarding adhesion tests, the ideal test would be the blister test [38, 39] (see figure 11b). The Pull-off test (see Figure 9a) in its current form, such as has been described in ASTM D4541, is also useful. It is certainly better (more reproducible etc) than the cross cut/hatch test. Wet adhesion can be measured with the pull-off test quite easily [40,41]

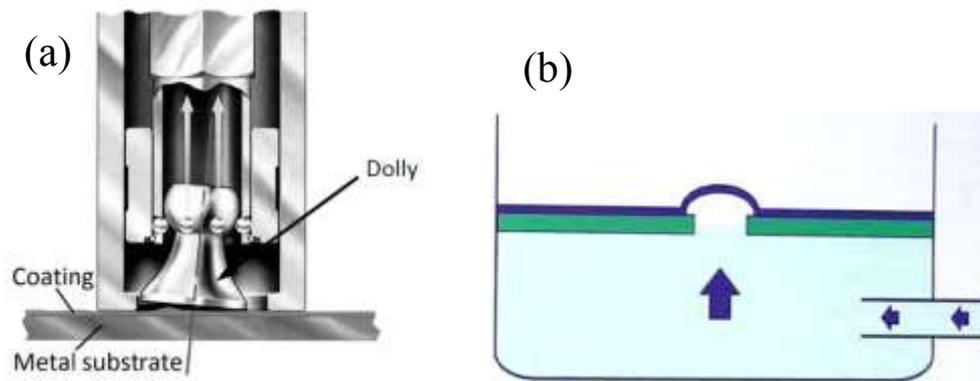


Figure 11 Schematic of (a) Pull-off and (b) blister test for measuring adhesion.

Water Uptake

This is conducted by using EIS to measure capacitance using the Brasher-Kingsbury [25] equation to obtain water uptake (Note that this is a complicated field, see ref [2] for further detail and for information on some experiments conducted in this area). The original equation, derived by Brasher-Kingbury in 1954, involves approximation and assumptions that are not valid in all cases and, more recently, the equation was reviewed by Sykes [42] and Castela et al [43,44] and modified equations were proposed.

Inhibitors

It is generally accepted that the main mechanism by which these operate is to help the maintenance of the metal oxide film at the paint/metal interface. But note that if these are acting effectively, one will see no corrosion of the iron metal even though one might measure a high permeability of the coating to ions (when a zinc rich coating is present is an example). However these type of compound whether added deliberately or just “arising” from the coating chemistry, can be seen as a second line of defence. So when the coating has broken down (e.g. developed defects and hence high permeability to ions) they operate to prevent attack and extend the lifetime. In the end they will “run out”. But it is still important to assess their effectiveness. This is a case where more sophisticated techniques like SVET and EIS on scribed samples will provide useful information. The detached film leaching tests discussed earlier have some relevance and when no free films are available, extraction could be performed on the coating (assuming single coat) when attached to the metal.

Metal alone

Although not strictly within the remit of this section, the state of the surface of the metal before the coating has been applied is very important and should be tested. As was mentioned earlier most coatings today are not surface tolerant. Taking plain carbon steel it should not be in an “active” state when the coating is applied e.g. the surface preparation method should not have reduced its corrosion resistance. For example, there is strong evidence [45] that grit blasting can decrease corrosion resistance by leaving particles of grit embedded in the surface. High pressure water blasting provides a much less corrodible surface. A simple potential time curve obtained from the bare metal (having been prepared in the chosen manner) in the anticipated environment will provide information. A more sophisticated approach would involve use of LPR or SVET.

Accelerated Laboratory tests

Immersion tests

These will be appropriate for coated metal (again we have in mind a carbon steel substrate although these tests can be applied to any metal substrate) which will be immersed either intermittently or continuously in practise. Either blanked off full panels are immersed in glass beakers or cells defining controlled smaller areas (eg 10cm²) are stuck on and filled. They are then left for various lengths of time (typically say 6 weeks) with the beakers/cells loosely covered but open to laboratory air. The degradation of the metal/ coating system can be accelerated if the temperature is raised or the solution is made more aggressive than might be expected in practise. In the case of testing paints for atmospheric exposure, the accelerating factor is associated with the provision of an unrelentingly aggressive environment rather than it being intermittent. The most common measurements that are made are that of potential and resistance. The former is not a totally reliable indicator although as said earlier if the paint is operating by a passivating mechanism this will be indicated by a high potential. The latter can be measured by any of variety of techniques discussed earlier such as ENM, Electrochemical Impedance Spectroscopy (EIS), Current Interrupter (C.I.) or DC resistance. For continuous monitoring of numerous samples Electrochemical Noise Method (ENM) in either the standard salt bridge electrode arrangement or one of the more practical electrode arrangements like single substrate [46] or no connection to substrate (NOCS) [47] would be the preferred method. There is an ISO standard on use of electrochemical noise which details in an annex how to apply the method to coated metal [48]. For acquiring mechanistic information about break down of paint in a lab environment, EIS and/or C.I are suggested. EIS has a standard associated with it [49–51]. So does C.I. [52]. But for quick ranking of coating with regards to their protective ability, DC resistance (or ENM) is recommended. And in order to differentiate high resistance systems more quickly, raising the temperature is helpful. The choice of which electrochemical monitoring method to use will depend on the particular conditions and preferences of the people carrying out the work.

An accelerated laboratory test that does not raise the temperature but uses instead DC polarisation (together with EIS) is the ACET method developed/invented by Suay, Garcia et al [53]. This test again has cells attached to coated metal and applies a 3V DC negative potential for periods of about half an hour. The system is then allowed to relax and the impedance measured. This is then repeated up to 10 times. This approach has some interest but the authors have some problem with the application of a high (3V) negative voltage, the like of which the coatings would not see in practise. Given the choice, the authors prefer temperature acceleration over the use of a severe bias potential.

Cabinet tests

These attempt, more closely than immersion tests, to simulate the outdoor condition in a laboratory environment, e.g. by closely controlling levels of ions, humidity, UV level and temperature. For paint coatings being used in typical (non-marine) atmospheric conditions exposure to hot/cold/UV conditions as defined in ASTM D5894 (dilute Harrison's solution (0.35% (NH₄)₂ SO₄/0.5% NaCl), UV, hot/cold cycle) [54] is recommended. Continuous salt spray 35°C, 5% NaCl is the most popular (e.g. ASTM B117) and is a satisfactory accelerated test for paints exposed to seawater or a marine environment in service.

Although samples in cabinet tests are not normally measured continuously it is strongly recommended that electrochemical methods (like DC or EIS or ENM) are used to assess the state of the samples during and after these type of tests. These will provide quantitative information and can be conducted using something similar to the quick drop test (see figure 12).

Normally, coatings are also assessed visually at the conclusion of both immersion and cabinet tests. They may also be analysed under the microscope to look for changes. Sophisticated analytical and characterisation techniques may also be used.

Outdoor Tests

Samples exposed externally

Samples can be placed in conditions of atmospheric exposure, continuous immersion or partial (intermittent) immersion in the field. These types of exposure tests are the ideal. But they take a long time. But if resources allow this, it is recommended. But again, in addition to visual examination, the protection afforded by the coatings should be assessed by electrochemical methods. Unless the samples are going to be brought back to the lab, probably DC resistance is the simplest.

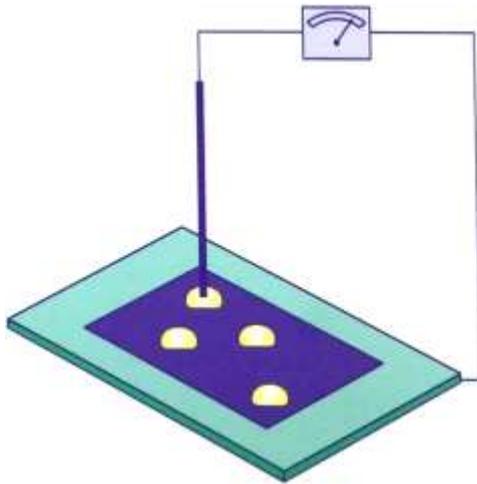


Figure 12 Quick drop test to check eg during an accelerated cabinet test , the homogeneity of resistance of a coated panel.

Real structures in the field

In the authors opinion, the best test for monitoring the state of the coating system on a real structure on-site is Electrochemical Noise Method [55–58]. For this to work effectively, dismantable sensors/probes are required and the single substrate (SS) or the no-connection-to-substrate (NOCS) electrode arrangements need to be utilized. There is a need for the production of a hand held, user-friendly instrument for conducting these types of electrochemical measurements. Another test which has been used successfully in the field is the Current Interrupter (CI) method [59]. Using either of these tests , one still needs to attend at the site and conduct measurement on the structure to get results. This is not always convenient. Work has been done using in-situ sensors and data communication via a modem to get electrochemical information using EIS and ENM on the state of coating at remote marine test sites [60]. There will undoubtedly be further development in this area with utilization of more modern data communication methods using wireless data communication protocols.

Further work

There is quite a lot of further work required in relation to mechanism, inhomogeneity, effect of surface preparation, adhesion testing, inhibitors etc. Some of these have been covered in another paper in this volume by Lyon et al [2]. Here we are just going to look at some unanswered questions in three areas: oxygen and water permeability, use of electrochemical techniques and accelerated testing.

- 1) Water and oxygen permeability

There is lack of in-depth understanding and study in this area. A useful paper was published by Thomas [58]. Earlier work suggested that oxygen permeability is less from high water activity solutions and higher from low water activity solutions [22]. Further work can be conducted using the techniques described in those two papers to determine criteria for O₂ and H₂O permeability. It is postulated here that both O₂ and water permeability are, at least to a certain extent, helpful to the formation and maintaining a passive state of metal substrate. But too great a permeability of either of these species will be deleterious. Work needs to be conducted to elucidate if a general optimum range of values exist and, if so, what is that range?

2) Electrochemical measurements

There is a need to investigate limitations to electrochemical techniques. For example, there appear to be situations when through-film resistance is high but the coating is either semi-detached (although not obviously) with no sign of corrosion; or the coating is detached with metal corrosion occurring under the coating. So further work is needed to see whether ENM or EIS can detect these situations either directly or indirectly (e.g. by inference). Secondly, in order to unify measurements, it would be useful to provide help for users by suggesting the best electrochemical methods for particular situations both lab testing and in the field. This would have to be based on extensive multi-laboratory investigations. On a more practical note, the development of a hand-held DC resistance meter would be very useful (this is not as simple as one might think)

3) Accelerated test

Further proof is needed to confirm that it is the degradation of I type coating that causes the resistance to fall in the field and in immersion tests and that this is accelerated by increased temperature. The current justification for this is based on work done in J E O Mayne's laboratory, University of Cambridge, fifty years ago (1960-66) where it was found unequivocally that the slow change (at room temperature) was accelerated by elevated temperature. However, more work is needed using modern coatings and also to correlate laboratory work with field experiments. Note that this is important as, at 75°C, degradation processes will occur at substantially faster rates, e.g. about 50 times faster, than at 20°C. We have suggested that if the value exceeds the T_g during testing, this is not critical at least in thermosetting systems [29]. No drastic change happens when coating passes through its T_g and the changes are often reversible. But this again is based on early studies and needs to be proven again for modern coating systems.

Conclusion

This paper has brought to the fore a number of “simple” (relatively) tests for the assessment of anti-corrosive paint coatings. This choice of tests, both those on free films and with the coating on the substrate, arises from a lifetime’s work in this area. A mechanism has been advanced based on the main purpose of a paint (as defined here) being the maintenance of an intact oxide film at the paint-metal interface. This has corollaries which suggest that adhesion, oxygen permeability and water uptake and are all important and need to be known. But there is probably a range of values that these parameters can take and, in general, the rate of corrosion under the coatings and the level of protectiveness are not controlled by any of them. The ability of the paint coating to produce inhibitive (or not) materials is also important and a simple leaching test to investigate that aspect has been outlined. Resistance (normally ionic) is still considered to be the paramount parameter and the emphasis in this paper is on the measurement of this. This “electrolytic resistance” is essentially the same value that Bacon Smith and Rugg measured some 68 years ago! At least four possible methods: DC resistance EIS, ENM and CI have been suggested to enable this value to be obtained. Which method to use is left to the reader. It is hoped that this paper has given a few pointers as to which is the most appropriate under which circumstance.

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