Changes during the Weathering of Polyurethane Water Pipeline Coatings

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Abstract

Aromatic polyurethane coatings are commonly used to protect steel water pipelines from corrosion while they are buried underground. However, during construction of a large pipeline project, coated sections of pipe may be stored above ground for extended periods and the polymer coating can suffer rapid and substantial changes in outward appearance due to sunlight, moisture, pollution, and heat. These changes in surface appearance can cause concerns about the ability of the coatings to function as a long term corrosion barrier although that protection is imparted by the whole thickness of a coating. The purpose of this investigation is to study the effect of UV, moisture and heat on four polyurethane coating formulations on both the visibly obvious appearance changes and on the likely corrosion protection. Candidate polyurethane coatings were subjected to laboratory weathering testing that causes very rapid degradation compared to natural environments. Quantitative testing of corrosion protection by electrochemical impedance spectroscopy has been done in concert with measurement of coating thickness loss and appearance changes (color, gloss). Appearance change is obvious and rapid but corrosion protection remains at very high levels. A longer term program is underway in which the same coatings are exposed to natural weathering in Florida and Texas so that the changes to the coatings in the real world may be correlated to the much more rapid results possible from accelerated laboratory testing.

INTRODUCTION

Steel water pipelines are most often buried in service and are protected against corrosion due to ground water by cathodic protection and thick organic polymer coatings. Coatings are often two-component polyurethanes that are made to cure very quickly in production and can be applied in thick layers that are very tough and withstand the mechanical stresses of being buried underground and subsequent ground movement. Other types of modern coatings are readily available but do not provide the same advantageous, economical balance as aromatic polyurethanes.

Pipelines typically have a design life of 50 years or greater and the corrosion protection from the pipe coating is paramount to long-term success of the pipeline. Unfortunately, a large pipeline project may involve coated sections of pipeline being stored, above ground, in a hot, moist climate for many months prior to burial. The appearance of the coating on the pipe deteriorates substantially under these conditions, which inevitably raises questions about the protective qualities of the coating.

Changes in the coating chemistry due to environmental degradation affect its appearance. Usually, the organic ingredients become yellow as exposure progresses and some pigments are bleached by the ultraviolet radiation often causing the visible color to shift considerably. Gloss is affected considerably by surface roughness, and so is affected by the material that is lost from the coating during atmospheric degradation. After considerable weathering some coatings may "chalk" which means that the surface has degraded to the extent that it is almost white and the surface has lost integrity and has become powdery [Wypych 1995].

The purpose of this investigation is to study the effect of UV, moisture and heat on four polyurethane coating formulations on both the visibly obvious appearance changes and on the likely corrosion protection. The results here are from exposure to standard (accelerated) laboratory weathering; an equivalent investigation is under way to obtain results from natural exposure for comparison. The results from natural weathering will be reported in the future.

Four coating companies contributed polyurethane coatings, BASF, Carboline (RPM), Futura (ITW) and LifeLast; results are presented for all four. None of the companies are identified by name in the results. A consistent color and symbol shape is used to represent data from each company in graphs. Discussion of the results is done only by reference to the symbol (circle, triangle, square or diamond) or color (blue, grey, orange and red).

BACKGROUND

Aromatic

The term "aromatic" refers to the unsaturated carbon ring structures in either, or both, the components that react together to form a polyurethane, in any use. The term "aliphatic" is used to describe a compound without these structures. Aliphatic materials do not absorb UV light nearly as much as aromatic compounds and are much more stable when exposed to sunlight in normal atmospheric conditions [Wypych 1995]. Both aliphatic and aromatic types of polyurethane provide tough mechanical properties and good barrier resistance to water. Aromatic compounds absorb more of the UV light in sunlight which damages the polymer structure, by photo-oxidation. The damage causes erosion and yellowing of the polymer much more quickly in aromatic compounds than in aliphatic material. However the advantages of aromatic chemicals are that they have significantly lower cost. They tend to have lower viscosity, and are often more reactive than typical aliphatic compounds. Thus aromatic polyurethanes are a better choice for a fast curing, 100% solids factory-applied coating, provided that its use does not entail long-term exposure to sunlight or other ultraviolet light. Unfortunately, photo-oxidation of organic polymers occurs more quickly if they become hot, and is often made worse by moisture and acid pollution which cause other forms of chemical degradation.

Color

Color is most often measured quantitatively by reference to a Cartesian coordinate system. The CIE 1976 L*a*b* color space [CIE 15:2004, Berns 2000] uses the L* co-ordinate to quantify where the color is on an axis that represents the change from black (= 0) to white (= 100), i.e. whether it is a dark color or a light color. The a* axis represents color on an axis that goes from green (negative) to red (positive); the b* axis goes from blue (negative) to yellow (positive). These three axes are at right angles to each other and one can represent a color by its coordinates in this space (L*, a*, b*), and one can represent a change or difference by the distance in this 3-dimensional space, using the same algebra that is used in other Cartesian spaces, e.g. x, y, z. Color difference, ΔE, is defined as the distance between two points, 1 and 2, in this color space and follows an easily recognized formula:

$$\Delta E = \sqrt{\left(L_1^* - L_2^*\right)^2 + \left(a_1^* - a_2^*\right)^2 + \left(b_1^* - b_2^*\right)^2}$$

Color and changes in color are readily measured by spectrometer and provide a non-destructive quantification of the changes due to degradation. As mentioned earlier, many polymers go yellow when exposed, so one should expect a change, Δb^*, in the b* quantity and thus in an overall color change, ΔE, as well.

Gloss

Gloss is a measure of the reflectance of a surface [ASTM: D523 - 14]. It is always evaluated by using collimated light from a specific angle and measuring the light reflected by the surface into a detector set on the opposite side at the same angle, i.e. the mirror like reflection. The greatest reflection of light occurs from a perfectly smooth surface. Gloss is very sensitive to surface roughness [Bennett 1961], so it decreases when a surface becomes rough due to degradation, because the rough surface reflects the incoming light into many directions away from the detector at the mirror (specular) angle.

The value of gloss is obtained by comparing the reflected light intensity to the reflectance of a very smooth glass standard. It is given as a percentage value, being the percentage of light that would have been reflected by the smooth glass standard, at a given angle. For example, a gloss of 90% does not mean that 90% of the light is being reflected, it means that the object is reflecting 90% of the light that the glass surface would have, under those conditions (and might actually be only be a few percent of the incoming light intensity in an absolute sense). A shiny surface will have a gloss close to 100% and a dull surface might only have a gloss of less than 5%. Gloss measurements are another non-destructive, simple method of quantifying visible changes due to degradation in a coating, as it becomes rougher due to the random erosion of its surface.

Electrochemical Impedance Spectroscopy, EIS

Electrochemical impedance spectroscopy measures the electrical properties of a coating film in terms of how much it impedes an electrical current to pass through its thickness. Impedance is determined by the ratio of voltage to current, over a wide frequency range. The direct current (zero frequency) impedance is the resistance. The measurement is done by using the metal substrate as the “working” electrode on one side and using an aqueous solution of a salt (usually sodium chloride) as the electrically conductive electrode on the other side. Usually, there is also a reference electrode in the system to ensure that the imposed voltage is not provoking corrosion itself. While a film is a good barrier it has a very high value of impedance, > 10^9 ohm, at low frequencies (~ 0.01 Hz). If a film has degraded to the extent that it allows a significant amount of water and salt to enter the coating which implies corrosion (electrochemistry) could occur on the metal substrate, those water and ions allow a significant current to pass and thus the film has a low electrical impedance. There have been many studies that confirm a high value of impedance means that the coating is providing protection. The technique and how the impedance is related to the dielectric properties of the coating material have been discussed in more detail previously [Croll 2015], and in many other places.

EXPERIMENTAL DETAILS

All of the panels and free films were prepared by Northwest Pipe using coatings supplied by BASF, Carboline (RPM), Futura (ITW) and LifeLast. The coatings were dark blue in accord with the most common coloration used by Northwest. The panels were purchased from Q-Lab Corporation, being SAE 1008 Cold Rolled Steel, blasted on both sides with a near white finish according to SSPC SP10. The panels were washed in methyl ethyl ketone prior to coating. Panels were masked to leave a bare metal contact for EIS measurements but sprayed on both sides and around the edges to prevent spurious rusting. Free films were prepared by spraying onto plastic sheet. All coatings and free films were sprayed to approximately 30 mils thickness. Enough panels were prepared that measurements could be made on 3 panels at each increment of exposure and a panel could be retained after each increment of weathering in case additional testing at that exposure was required.

Accelerated exposure was done according to ASTM 4587 (QUV A type), cycle 1: UV + condensing humidity: 8 h UV of 0.83 W/(m^2·nm) at 70 ± 2.5 ºC (158 ± 5 ºF) and 4 h condensation (dark) at 50 ± 2.5 ºC (122 ± 5 ºF), repeated continually. The chamber calibration is checked every 400 hours. Testing intervals were at 1 week, 2 weeks, one month, 3 months and 6 months.

Gloss measurements were made using a Gardco Statistical Novogloss Glossmeter and the color measurements with a MacBeth Color Eye 7000 using the D65 (daylight) illumination [CIE 15:2004]. For gloss, the data are averages taken from 3 panels with 5 readings on each panel. The high number of replicate readings was in order to diminish the effect of the surface texture remaining after the coatings had cured. Color measurements were the average of 3 places on each of 3 panels for each formulation.

Electrochemical impedance spectroscopy was performed with a Gamry Reference 600^{TM} potentiostat connected to a standard desktop computer using an aqueous electrolyte of 3% sodium chloride.

In the QUV chamber, panels are mounted facing inwards at an angle of approximately 70-75 degrees. During exposure, moisture condenses on the panels and runs down, thus gently removing the material that is very loose. No other cleaning process was used. Free films made of pipeline coatings have enough rigidity that they can be placed in standard exposure panel holders and held in place with the normal spring clip. These were used to determine weight loss due to erosion during degradation because there was no contribution to the sample weight from a metal panel substrate. A normal analytical balance could distinguish the weight change after each increment of weathering. Contact with the surface of the samples was minimized when handling in order not to rub any material off.

RESULTS AND DISCUSSION

Overall Appearance

The images below are of a representative sample that had 1 month exposure in the QUV accelerated weathering chamber. The images were made on a flat-bed scanner. The change in color can be seen in each case by comparing the masked regions to the rectangular area towards the left hand side that was exposed. These were panels that were tested with EIS and the size and location of the EIS cell can be discerned. The bare steel area at the right hand side is for making an electrical connection to the metal for EIS, and is taped over while the panel is being exposed.

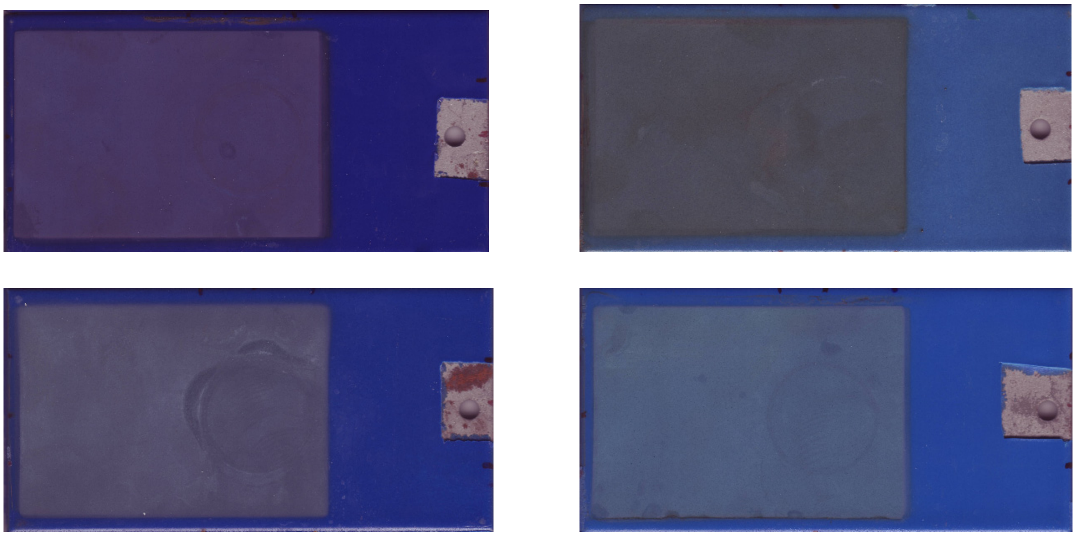

Figure 1. Images of each of the four coatings on steel panels, showing how appearance has changed after 1 month in QUV. The edges and end are covered by the panel holder (and some tape) during exposure and thus did not degrade.

The initial colors are not identical, but one can see that the changes are visually obvious in each case.

Gloss

Results are separated into those taken at 20 degrees, 60 degrees and 85 degrees. The 20 degree is most representative of normal observation and is not very sensitive to the surface texture imparted during the spraying of the coatings. Grazing incidence, 85 degrees, is very sensitive to unevenness in the surface and is not usually useful for studying changes due to degradation.

The gloss has diminished in all cases to a low value after 6 months of QUV exposure. This is very characteristic of gloss measurements after weathering and typical of such coatings since they are aromatic polyurethanes. The four coatings had appreciably different surface texture which influenced the trends in the data at 60 and 85 degrees. In all cases, gloss has deteriorated to very low values and cannot show any further change after more exposure. One month was sufficient to diminish the 20 degree gloss readings to essentially zero.

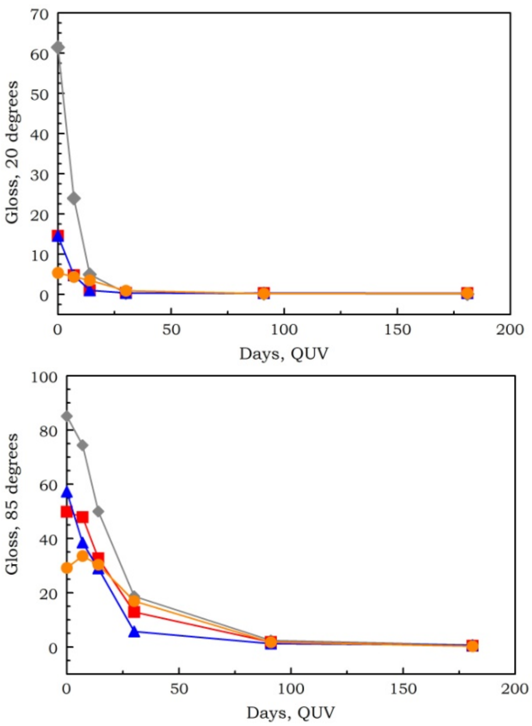

Figure 2. Trends in gloss with the exposure period in QUV accelerated weathering. For each coating the data are averages taken from 3 panels with 5 readings on each panel.

Color

Color measurements are less sensitive to surface texture. The results in figure 3 are from 3 panels and 3 places on each panel. Again, these are typical of the rapid change to be expected in aromatic polyurethanes.

ΔE is the composite change incorporating the three components of color; lightness (L*), red-green (a*) and yellow-blue (b*). Decreasing L* means that the coatings are darker. Increasing a* shows that a color is becoming more red whereas a negative change indicates that the color is shifting towards green. Yellowing is shown by the results for *Δb** where the increase in value is consistent with the behavior of aromatic polyurethanes (reduction in b* would mean that the color is becoming more blue).

In all cases, the color changed substantially after exposure for one week, but less thereafter. These coatings all changed color faster than they lost gloss. The change in overall color, *ΔE*, is dominated by the yellowing and the change in lightness. Changes in color coordinates, as conventionally measured, are not independent of each other. The change in lightness will be due to the increase in yellowing, making the coating darker, and due to the reduction in gloss because the coating is not reflecting as much light and thus becoming darker. Again, the changes in appearance, color in this case, have reached a point where they do not change significantly and will not be indicative of further degradation as the coatings continue on exposure.

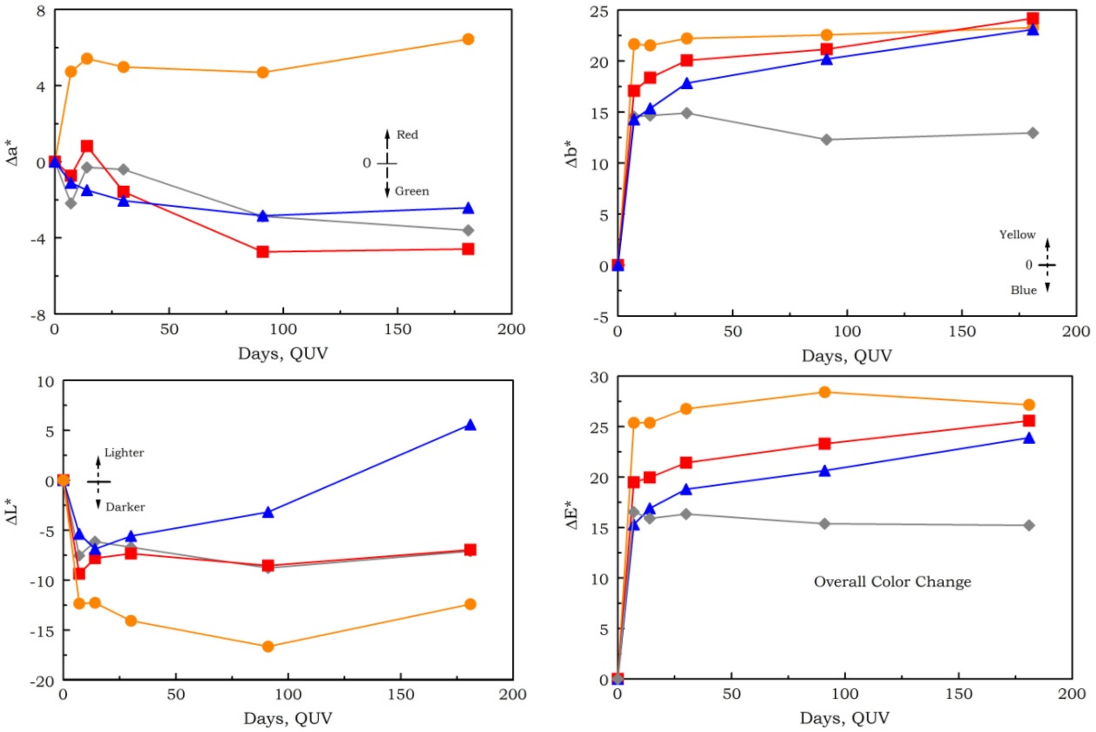

Figure 3. Color change after exposure in QUV accelerated weathering. CIELAB color values here are obtained using the D65 (daylight) spectrum.

Weight Loss

Weight loss was measured on free films that were exposed at the same time as the other coating samples on metal substrates. The weight loss can easily be measured by analytical balance after each increment of exposure. The area exposed is 3.75 x 2.5 inches (95.25 mm x 6.35 mm) for each sample. Each coating has three samples exposed. Weight loss is determined by an analytical balance and then converted into a thickness reduction by assuming a coating density of 1.2 g/cc, see figure 4 which shows the average over the 3 samples of each formulation. As an example, after 1 month coating films had lost approximately 0.1 grams which is readily determined on an analytical balance that weighs to a resolution of 0.0001 grams.

Weight loss continues with exposure although the changes in gloss and color seem largely complete. All of the coatings continue to degrade and be eroded. If a typical coating was sprayed with a dry film thickness of 30 mil (762 µm), the samples here have lost approximately only 8% (~ 60 µm) of their thickness after 6 months (~181 days), or approximately 0.33 µm/day. Weight loss, or reduction in thickness, is a useful method of evaluating degradation and often follows a more or less linear trend throughout an exposure [Bauer 1996, Gu 2001, Wypych 1995].

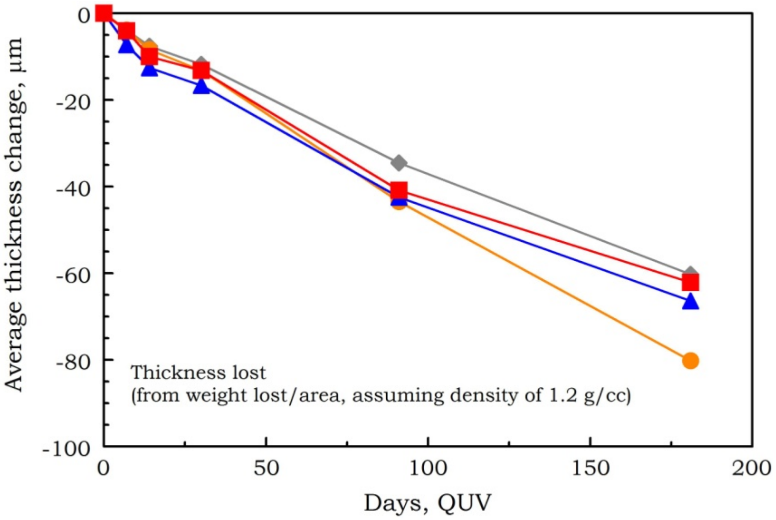

Figure 4. Thickness reduction calculated from weight loss of free films in QUV exposure. Density of all the coatings was assumed to be 1.2 g/cc. 25.4 µm = 1 mil.

Pipeline coatings are very much thicker than coatings used in other decorative or protective applications, where the dried film thickness is more often 2 mil (50 µm) approximately. In that case, these thinner coating formulations would have been worn to almost nothing after 1 month in the QUV and would have failed at that stage. In contrast to the thick pipeline coatings, the time scale for the change in gloss and color, in such thinner coatings, would have more closely matched the time scale for complete failure.

For these typical pipeline coatings in the accelerated weathering here, the loss of gloss and the change in color, which are surface or near-surface properties, have ceased to correlate with the continuing reduction in thickness, because the coatings are so thick.

Electrochemical Impedance Spectroscopy, EIS

'Bode' plots are graphs showing how the impedance of a coating varies with frequency. The axes are usually logarithmic in order to accommodate the large variation of the impedance over the several decades in frequency of the voltage.

Figure 5 compares the 'Bode' plots of the unexposed material with the response of the coatings after 6 months accelerated exposure. For each of the 4 coatings, there are 3 replicate panels being tested. Almost all of them have very high impedance which is the result of being thick, protective films.

Open symbols denote the data from the initial, unexposed coatings; the solid symbols show the data after 6 months exposure in the accelerated testing where some slight changes are apparent. The data taken at intermediate exposure intervals is not shown because it is indistinguishable from the initial data on these graphs.

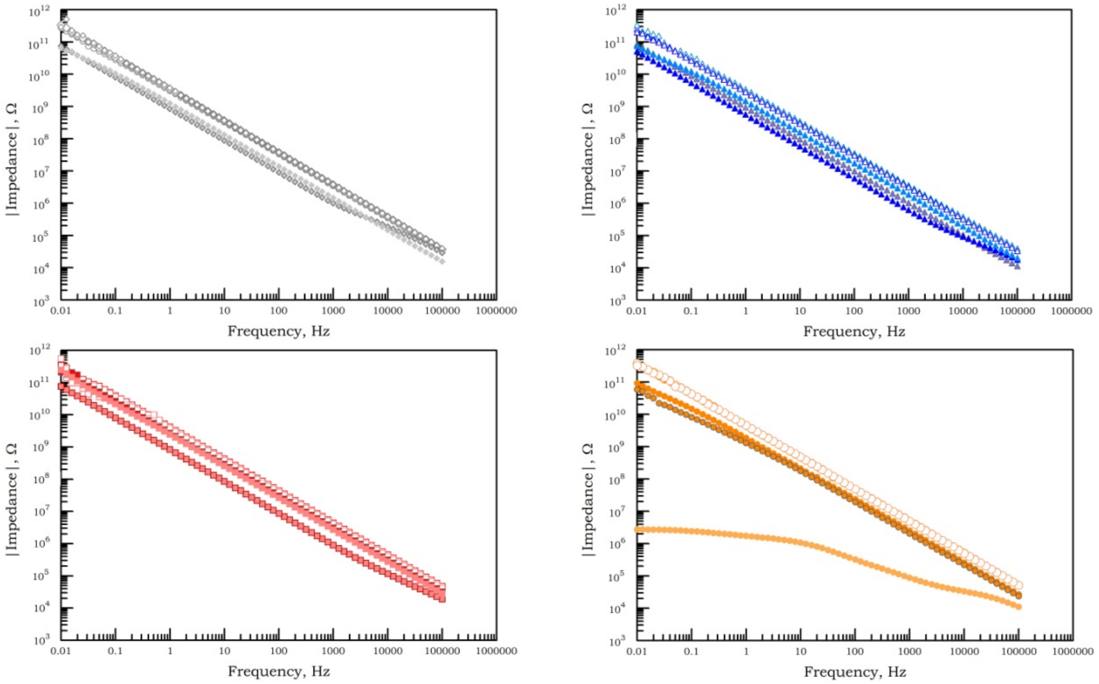

Figure 5. EIS results, all three samples of each coating. Symbols and colors show impedance data from the same coating formulation. Impedance of the unexposed samples is shown by the open symbols (higher values on each graph); impedance values after 6 months are shown using filled symbols.

None of the samples show any visible signs of corrosion. However, one of the orange (circle) samples shows a substantial loss of impedance across the frequency spectrum. All the other samples continue to have very high impedance, especially when one considers that a low frequency (0.01 Hz) impedance of greater than 10^{9} ohm is considered to indicate a protective barrier coating.

Impedance is determined by dielectric material properties and is also proportional to the thickness of the material remaining. If the material properties of the coatings in this study are not changing due to chemical change, the impedance will be reduced by 8% due to their loss in thickness. A change of only 8% would be very difficult to perceive on the logarithmic axes in figures 5.

Another approach to using the EIS results is to follow how the impedance, recorded at a very low frequency, changes with the length of exposure. Usually, the impedance at 0.01 Hz is taken to represent a DC “coating resistance” which has been used to follow the decline of a coating to failure. There are a number of examples of this in the literature where the failure point of the coating is considered to be when its resistance falls to be the same as a layer of rust on the metal. Often this point is at an impedance of 10^{4} to 10^{6} ohms. In fact various authors maintain that coating resistance follows an exponential decay with exposure time and so one can extrapolate declining impedance to a point when it becomes equal to only a layer of corrosion products, thus defining a service life [Su 2015, Bierwagen 2003]. Figure 6 shows the trend in impedance at 0.01 Hz of all the 3 replicates of all 4 coating formulations.

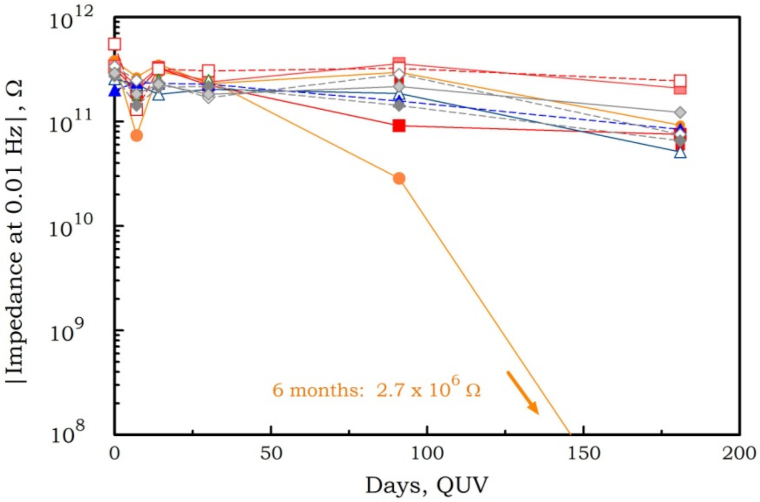

Figure 6. Coating impedance at 0.01 Hz, i.e. "coating resistance", of all the replicates of the 4 coatings formulations. The color of the symbol and connecting line indicates the coating the coating formulation.

The low frequency impedance of most of the samples has declined only slightly. Some reduction is inevitable after this period of accelerated weathering, but the impedance values at this low frequency remain high and indicative of good barrier coatings.

As figures 5 and 6 indicate, only one orange (circle) sample exhibits obvious signs of very reduced impedance. This sample also showed a reduced impedance after 3 months exposure. The change in this sample is probably the result of a defect in the coating arising from contamination or other imperfection in the application process. The fact that 2 other examples of the same formulation are doing well would indicate that there is no systematic problem yet apparent with the formulation.

SUMMARY

Accelerated weathering has been used in an effort to determine whether the visible changes in appearance of the pipeline coatings can be connected with changes in corrosion protection. It is well known that accelerated weathering is very aggressive, but does not predict the failure modes seen in natural exposure. However, it does indicate whether a material has a weakness in these artificial, aggressive conditions.

Gloss and color measurements show large, rapid changes in appearance that are consistent with expectations for the aromatic polyurethanes used for coating pipelines. Color changes, principally due to yellowing and becoming darker, reached a plateau slightly faster than the gloss decreased to zero. Throughout exposure, the coatings continued to be ablated, i.e. lose mass and thickness, at a consistent pace indicating that degradation was continuing unabated, after the appearance had ceased to change.

Apart from one case of possible application defects, after 6 months there does not seem to be any change in corrosion protection as determined by EIS impedance, although the appearance has changed considerably.

Evidently, although the coatings' appearance has deteriorated significantly there is no similar reduction in corrosion protection on the time scale of these experiments. Appearance change occurs in the outer layers of a coating whereas the whole thickness contributes to the barrier properties for corrosion protection. Weight loss continues at a more or less consistent rate in these exposures but they have only lost a minor percentage of their thickness here which will not affect EIS results discernibly. Much more extended exposure may eventually cause a loss in corrosion protection, but only when a substantial fraction of the coating has been eroded. Although it may not be possible to measure in service, weight loss during exposure may be a much better indicator of loss in corrosion protection than appearance changes.

Although the detailed changes in appearance were different for each of the coating formulations, they all changed their color by very similar amounts and their change in weight is very similar. At present, there is nothing that suggests one formulation is inferior or superior to the others. A matching program to expose and test these materials under natural conditions has started and will be reported in the future.

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