Gloss and Color Changes during Exposure of Polyurethane Coatings for Steel Water Pipes and Their Possible Link to Long-Term Corrosion Protection

Stuart Croll[1]; Chunju Gu[2]; Vinod Upadhyay[3]; and Brent Keil[4]

[1]North Dakota State Univ., Dept. of Coatings and Polymeric Materials, Fargo, ND 58108-605. E-mail: Stuart.Croll@ndsu.edu
[2]North Dakota State Univ., Dept. of Coatings and Polymeric Materials, Fargo, ND 58108-605
[3]North Dakota State Univ., Dept. of Coatings and Polymeric Materials, Fargo, ND 58108-605
[4]Northwest Pipe Company, 5721 SE Columbia Way, Suite 200, Vancouver, WA 98661. E-mail: bkeil@nwpipe.com

ABSTRACT

During large pipeline projects, pipe sections can be kept above ground for many months before burial. Thus, their corrosion protective polymer coating, commonly an aromatic polyurethane, may be exposed to ultraviolet solar radiation and high temperatures that were not anticipated for its ultimate service, in the ground. The gloss of such coatings deteriorates very rapidly and the color of the coating changes a great deal quickly which can lead to concerns about their remaining corrosion protective ability. Previous evaluation at 6-month intervals of field exposure in Texas and Florida showed that these changes in appearance occurred during the first 6 months. An expanded study wherein the coatings were evaluated at much shorter intervals, in Texas, shows that color changes rather faster than the gloss, within one month approximately, whereas the gloss diminishes over 3 months. Interestingly, both the color and gloss properties change in a pattern described very well by an exponential trend. This pattern of deterioration can be derived easily using a very simple assumption that ultraviolet light, water molecules, etc. from the environment cause their damage at random times and locations. This approach shows there may be links between properties such as weight loss and gloss loss and, in this case, that corrosion protection would diminish very little in these very thick polyurethane films. In fact, the most recent results from extended field test exposure sites in Florida and Texas show that the corrosion protection of these coatings remains intact.

INTRODUCTION

Two-component, aromatic polyurethane coatings used to provide corrosion protection for water pipelines are chosen for their economic balance, their resistance to the stresses of being buried and their ease of rapid application in thicknesses that provide a long-lasting barrier to ground water etc. This coating chemistry is susceptible to photodegradation, but we must remember that durability against extended exposure to sunlight is not part of the system design. Occasionally, coated sections of pipe are left exposed to weather for extended periods and naturally suffer extensive loss of gloss, yellowing etc., see Figure 1, and thus raise questions about the likely level of corrosion protection. Previous experiments on accelerated and natural exposures in Texas and Florida for 12 months [Croll et al. 2017] has shown that the corrosion protection remains intact even though the gloss loss is complete and the color has changed considerably.

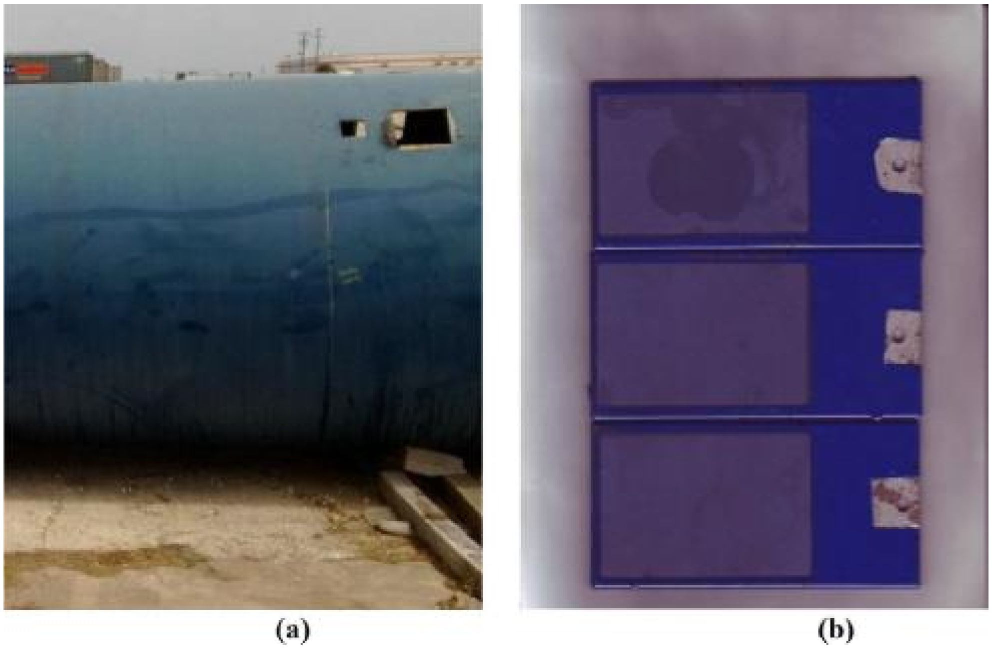


Figure 1. (a) Section of coated pipe, originally dark blue, after 2years storage in Texas. The top has lost gloss and changed color but, in the shade, the bottom has retained its appearance, (b) coated steel panels after 3 months of accelerated, QUV, weathering. The exposed area has changed but the ends and edges, where the coating was shielded, have not.

Further exposure results confirm that the corrosion protection remains for at least 18 months. Such results are reassuring but do not provide any mechanistic link between appearance and corrosion barrier properties.

This study includes an expanded exposure series with more frequent intervals so that the kinetics of gloss loss can be measured as well as the rate of material loss, so that a simple model that links them and the corrosion barrier properties can be evaluated. This model provides an explanation of how gloss quickly decreases to zero although material loss continues and corrosion barrier properties remain unaffected. Ultimately, an understandable causal link is more satisfactory and useful than several series of data points that are apparently correlated.

Five coating companies contributed coatings, BASF, Carboline (RPM), Futura (ITW), LifeLast; and Valspar (Sherwin-Williams). All of these coatings were pigmented to be dark blue, consistent with much of the pipes manufactured by Northwest Pipe. 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.

EXPERIMENTAL METHODS

Gloss, color, weight loss and electrochemical impedance spectroscopy measurements, EIS, were taken at 6-month interval exposures in Florida and Texas. Experimental methods have been described in detail before [Croll 2016] and were followed exactly in the most recent measurements.

Unfortunately, gloss loss and yellowing reached their final values very quickly, within the first weathering increment of six months, and thus no details of the rate of change was available.

Fortunately, there were enough samples remaining of two coatings that could be sent to Texas for an expanded program where weathering was done in shorter increments over a few months. This data is given here in addition to the other data, and is referred to as the expanded program. The expanded program allowed the kinetics of gloss loss and yellowing to be clarified.

Gloss and color measurements on samples that were previously exposed in accelerated weathered or in the Florida or Texas were taken from the same location on the same coated panels at each increment of weathering. That was not possible for the expanded exposure program in Texas where the data from each increment of weathering was measured on different panels. Thus the data from this part of the project has more variations than results from the others. When panels are exposed for significant periods in the natural environment they may be affected by circumstances that are difficult to control. For example, color, gloss and weight measurements on the panels from the weathering are affected by dirt and other problems and the process chosen to clean the surfaces. There was a strong storm that dislodged the panels during exposure in Texas. The greatest effect was that several of the free films that were used for the weight loss experiments were broken and had to been cleaned vigorously, which changed their weight significantly and so there is a discontinuity in their weight which was not connected with general degradation. This has been noted on the graphs of weight loss (thickness loss) data.

KINETICS OF COATING DEGRADATION

Pipeline coatings are commonly composed of aromatic polyurethanes that absorb ultraviolet radiation which causes the polymer to degrade and lose gloss and be oxidized and become more yellow. If one examines the solar spectrum at the Earth' surface [ASTM G173 2012], one finds for example, that around 350 nm in the near UV region, approximately 1 photon of this wavelength is arriving every second, on each square nanometer of surface. Thus there are a huge number of opportunities for photodegradation. Similarly, air at sea level contains ~ 5×10^{24} molecules/m^3 of oxygen and ~ 4×10^{23} molecules/m^3 of water at 50% relative humidity and 25 °C [CRC Handbook 2014]. Degradation is not limited by the availability of a sufficient number of UV photons, or molecules of oxygen and water.

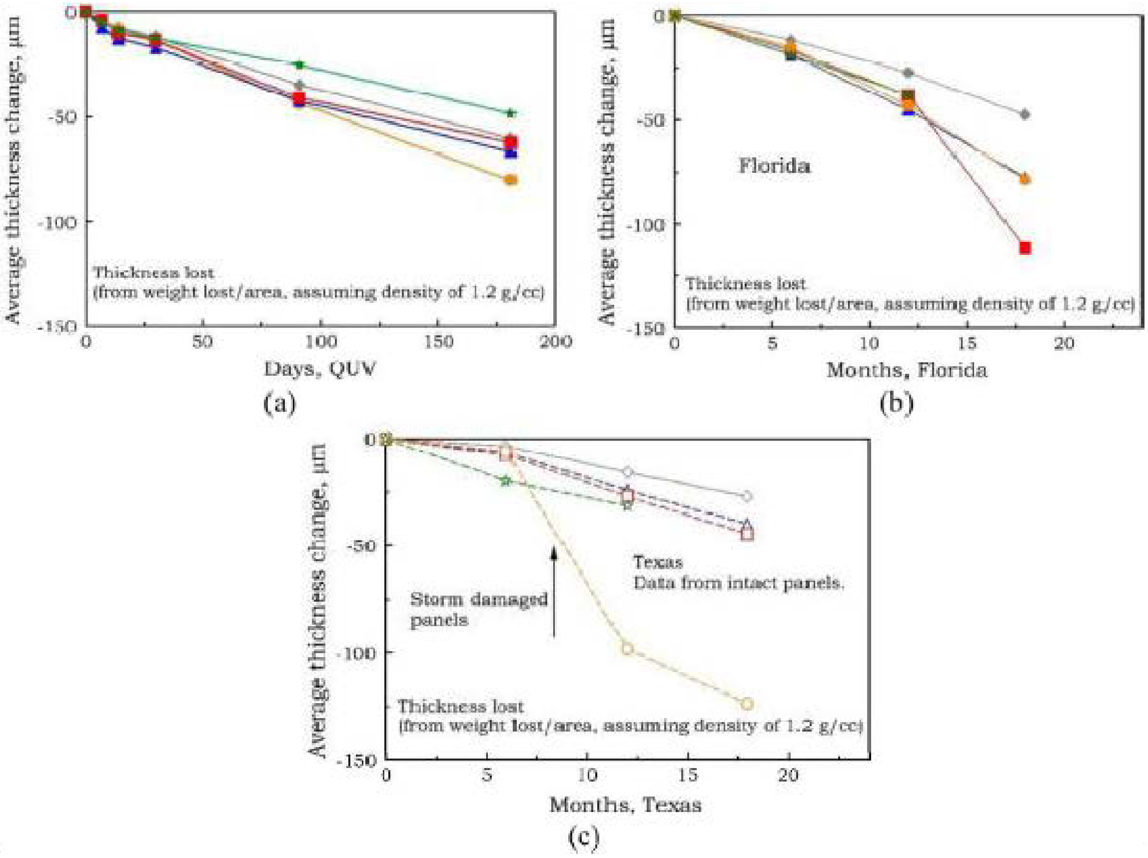
The focus here is on photooxidation by UV photons since that is the mode of failure in aromatic polyurethanes exposed to the natural environment. However, the approach can easily be translated to describe chemical attack by a large number of aggressive molecules. The environment is described by the flux of photons and the material by the fraction of those photons absorbed and the quantum yield for damage. This approach uses average parameter values to represent the environment and material and thus represents the most likely outcome. Statistical variation in exposure and absorption and thus outcome is a natural part of this model and the real world and can be deduced from the statistics of random phenomena [Croll 2007, 2017].

Degradation starts and progresses on the exterior surface of a material [Fechine (2004)]. At the surface:

$$\begin{aligned} N(t) &= \text{ Average number of fragments removed } (\text{or other damage}) \\ &= \text{Flux of photons} \times \text{concentration of degradable bonds} \\ &\quad \times \text{Probability of Absorption and bond scission} \\ &\quad \times \text{Time } (t) \\ &= \phi .\, N(0) .a.t \\ &= K\,(= \text{constant}) \times t \end{aligned} \tag{1}$$

The symbols are defined by the order that they occur in Equation 1. The kinetics assume that the degradation immediately affects the whole exposed surface, which certainly seems to be the case in these aromatic polyurethanes. This model assumes that the exposure period is much longer than any diurnal or other fluctuations and so utilizes average values of parameters. One could readily express exposure in terms of radiation dosage, ϕt, instead of time. Equation 1 assumes that if a degraded fragment leaves then the material underneath is similarly assaulted and so there is no change in the degradation rate caused by a change in concentration and so follows simple zero-order kinetics. One could measure all parameters readily. A more complete model would include Beer's law or the Kubelka-Munk model to account for the penetration of radiation and the concentration of absorbing species or pigments etc, but that level of complexity is not required here.

If each fragment removed caused the same reduction in thickness via a characteristic linear size of ε, then the thickness would decrease with exposure as $\varepsilon.N(t) = \varepsilon Kt$.



(a) (b)

(c)

Figure 2. Thickness reduction with time, (a) accelerated, QUV, exposure, (b) Florida exposure, (c) Texas exposure. The results from Texas show when samples were damaged during exposure.

Loss in thickness

This simple approach has that mass loss, or the equivalent thickness reduction, should continue at a constant rate with exposure. Weight loss, provided that it is large enough to be detected, would be a simple measure of durability but is not as common an approach as measuring appearance properties, such as gloss or color. Coatings that are very durable in sunlight, for example automotive coatings that are designed to have excellent appearance for 10 years, show very little mass loss which means this measurement in not universally useful. However, it proved possible for the coatings studied here. Figures 2a, b and c, show the reduction in thickness for the coatings measured in accelerated weathering and in Florida and Texas exposures.

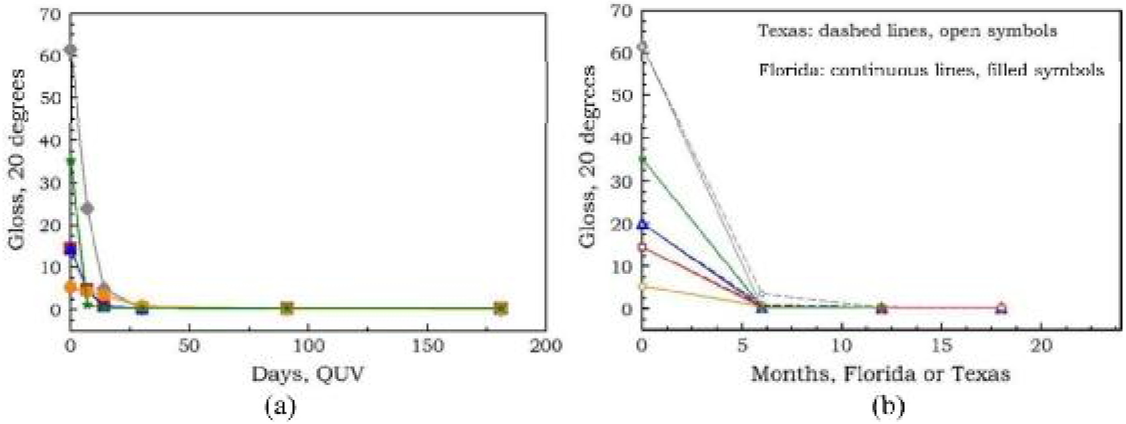
The graphs indicate that the thickness reduction is indeed approximately linear, although the data from natural exposures is more prone to experimental variations due to accidents and methods of dirt removal.

Gloss Loss

Gloss is the specular reflectance of a surface. Quantitatively, it is measured relative to a standard glass surface and is very often used to monitor durability of a material since it is a rapid and easy measurement. It is possible to use this model to calculate the likely loss in gloss. Loss in gloss is caused principally by a random loss of material that leads to an increase in surface roughness. Roughness can be expressed as the root mean square deviation in height of the surface, and thus can be derived from the standard deviation in the average number of polymer segments removed anywhere [Croll 2007, 2017]. This then can be combined with a long standing theory that relates loss in reflectance with surface roughness [Bennett 1961] to give an expression for the relative loss in gloss from its initial value as presented in Equation 2.

$$R_s\left(t\right)/R_0 = \exp\left[-\left(\frac{4\pi\cos\varphi}{\lambda}\right)^2 kt\right] \qquad (2)$$

$k = K.\,\varepsilon^2$ where ε is the characteristic (linear dimension) of the fragment size whenever material is lost (Equation 1)
$R_s\,(t)$ = specular reflection of the rough surface,
R_0 = reflection of a perfectly smooth surface of the same material,
φ = gloss measurement angle,
λ = wavelength of the illumination.



(a) (b)

Figure 3. 20 degree gloss loss with time, (a) accelerated, QUV, exposure, (b) Florida and Texas exposures (together).

Thus Equation 1, which has loss in material continuing linearly with exposure leads to

Equation 2 which predicts that gloss diminishes exponentially with exposure time (in simple cases). Gloss measured at 60 or 85 degrees is influenced strongly by shadowing and masking [Bourlier 2002] due to application surface texture, but the gloss loss measured at 20 degrees can be used to test Equation 2. Figure 3 shows the gloss reduction measured under the same circumstances as the weight loss in Figure 2.

Gloss is diminished greatly as soon as the surface height deviations, i.e. roughness, becomes comparable to the wavelength of light (wavelength of green light is 560 nm). It is clear from Figure 2 that material loss continues throughout the exposure and so the material may be losing its protective capabilities, although the gloss does not change further.

In these exposures, gloss loss happens very quickly so there are too few data to test whether the curves are genuinely exponential. However, the expanded exposure series conducted at the Texas site provides a better opportunity, see Figure 4. The curves on the graphs are simple exponentials where both have the same time constant, τ, of 20 days.

$$Gloss(t) = Gloss(0).\exp\left[-\frac{t}{\tau}\right] \tag{3}$$

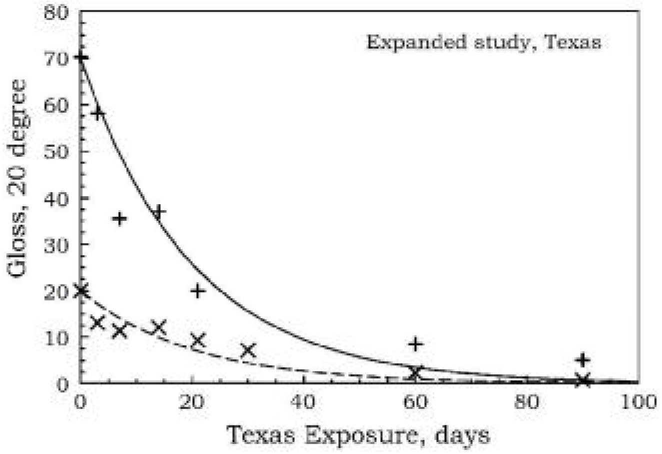


Figure 4. Gloss loss, at 20 degrees, of two coating formulations during exposure in Texas. The continuous curves are simple exponentials with the same time constant of 20 days.

The time constant of 20 days is very short compared to the first weathering increment initially used in both Florida and Texas and demonstrates why the initial program of exposures was not discriminating. Unfortunately, continued degradation cannot be monitored by gloss loss since it had decreased to zero. While continued material loss can be used to calculate gloss (although it predicts zero gloss), the very low value of gloss cannot be used to calculate material loss reliably.

Taking a typical thickness loss in Texas to be 30 μm over 6 months and comparing that to the time constant of 20 days for gloss loss, provided that the characteristic size, ε, is the same in both cases, some simple arithmetic shows that the value of ε that satisfies both behaviors at the same time is approximately 0.7 nm. This seems reasonable for the size of a molecular fragment that is lost from the surface of a coating, e.g. by leaching and so one can say that the simple model is plausible.

Yellowing

Yellowing with exposure can be quantified using *Δb**, in the Commission internationale de l'éclairage, CIE, L*a*b* coordinates. It occurred even faster than gloss loss in the extended Texas exposure, as has been seen before [Croll 2016] in the artificial weathering and in the natural weathering. The curves on Figure 5 are simple exponential curves:

$$\Delta b^*(t) = \Delta b^*_\infty \left[1 - \exp\left(-\frac{t}{\tau}\right)\right] \tag{4}$$

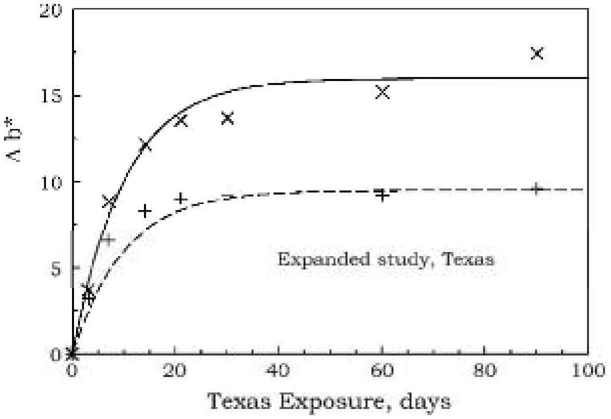


Figure 5. Increase in yellowing in the expanded Texas exposure. Both curves have a time constant of 10 days.

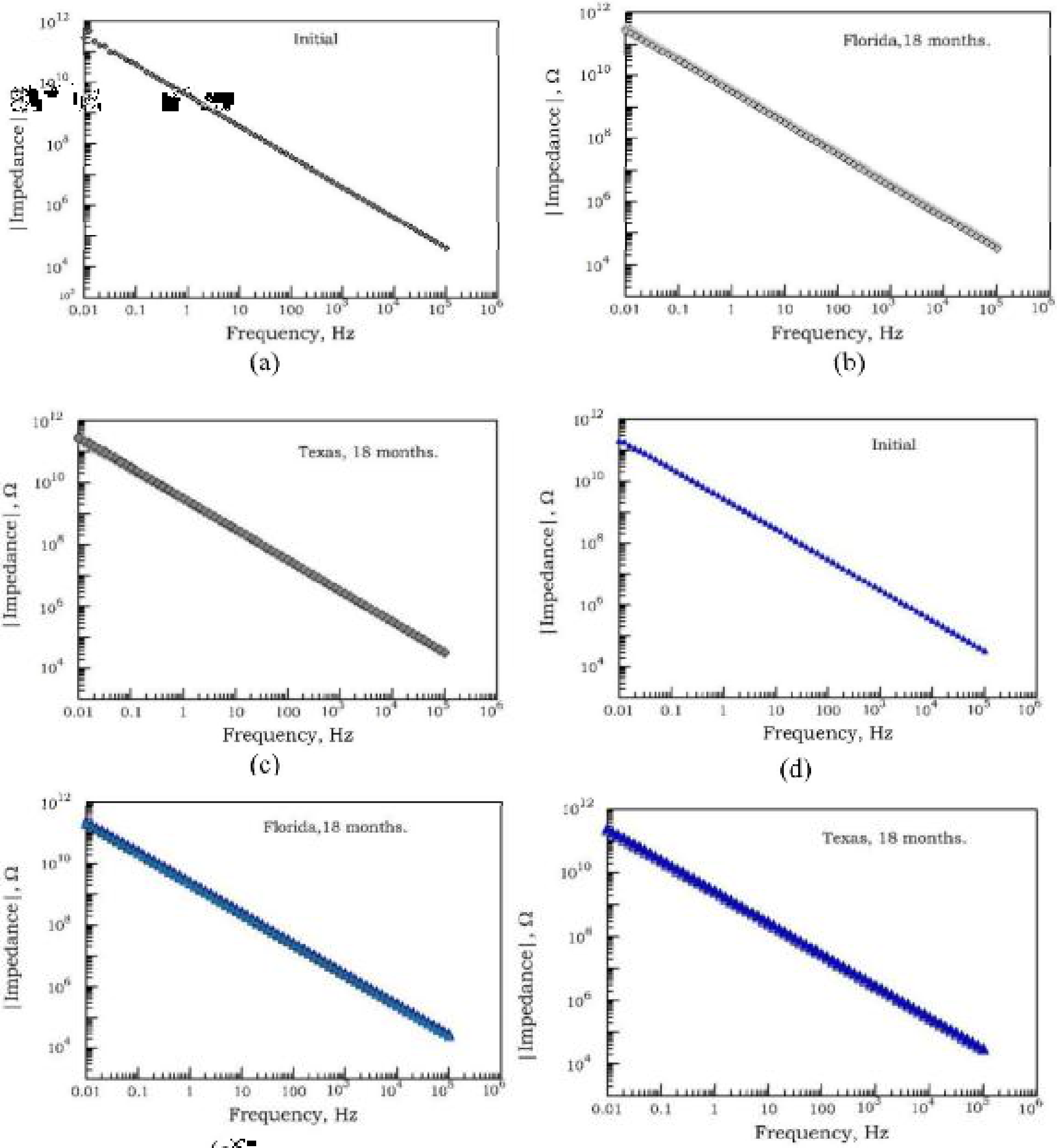
The starting color in all cases was dark blue, so exposed areas of the coatings became greener as the blue color was adulterated by the yellowing.

At present it is not known whether yellowing can be related to the model for material loss, so Equation 4 is not derived from the earlier model or equation, but used only to better quantify the underlying rate of yellowing. In the extended Texas program the characteristic time constant of the exponential increase in yellowing was 10 days in both cases which is faster than the gloss loss. This is consistent with data published before from this exposure series where again the exposure increments were too large to quantify the comparison. However, the consequence is that yellowing ceases to represent the true state of coating loss, even faster than does gloss.

Quantifying the degradation of a coating by its appearance is a natural and convenient approach. However, both gloss and yellowing of these aromatic polyurethanes change very quickly and then cease to exhibit any change after a very brief exposure, but we can see that mass continues to be eroded, Figure 2, as the exposure continues. Thus there are grounds for concern over the corrosion protective qualities of the coatings, which are designed to be barriers by virtue of their thickness so that water and salts cannot penetrate and corrode the pipe underneath.

Corrosion Barrier Performance

The barrier properties of a coating can be quantified by the modulus (absolute value) of electrical impedance, Z, measured by electrochemical impedance spectroscopy where the impedance is measured between a conductive electrolyte on the top of a coating and the metal substrate underneath. Materials have behavior like a resistance, and another behavior like a capacitance. The impedance due to both behaviors depends linearly on the thickness of the coating [Croll 2015]. Thicker coatings give higher values of impedance which indicates that they should be better barriers.



(a) (b)

(c) (d)

(e) (f)

Figure 6. Electrochemical impedance as a function of frequency before and after 18 months exposure. (a), (b) and (c) are results from one coating and (d), (e) and (f) are another example.

Polyurethane coatings that are used to protect steel water pipelines are usually >800 µm (~ 30 mil) thick. Depending on the environment, and the exposure period, these coatings become somewhat thinner, as quantified in Figure 2 which shows that they might lose 50 μm after 18 months in Florida or 30 μm after 18 months in Texas. This is approximately 5% of the thickness of the coatings, so that the impedance of the coatings would be similarly reduced. The EIS impedance of two of the coatings, as examples (they are all very similar), after 18 months in both Florida and Texas is shown in Figure 6 with their initial impedance for comparison. There is no perceptible change either between initial and exposed materials, or between several exposed samples of the same formulation.

These graphs are logarithmic to show all the data that spreads over many decades of frequency. If impedance is reduced by 5% due to loss of thickness, it would not be apparent on these graphs. In addition, from many people's experience, a coating is presumed to remain protective if its impedance is greater than 10^9 ohms at low frequencies. The impedance of all these coatings is approximately two orders of magnitude greater than this. If these coatings fail to provide corrosion performance, it will not be due to overall thickness loss from general degradation when exposed. Failure of the barrier properties is more likely to arise from a defect in the coatings caused either by application or subsequent damage.

SUMMARY

Once a coating has completely lost its gloss and yellowed (or chalked) concerns arise over its continued ability to provide corrosion barrier protection for the underlying metal pipe. Experimental data, on the aromatic polyurethanes that are typically used, show that the appearance deteriorates and very quickly reaches a state that does not change much although degradation, as measured by material loss, continues unabated. Corrosion protection determined by the electrochemical impedance demonstrates that the coatings' performance remains essentially unchanged and so the coatings remain good barriers. The experimental exposure series on these pipeline coatings shows that appearance changes, even though they change greatly, are not predictors of corrosion protection for these coatings. Any failure of corrosion protection would occur due to another process, e.g. an accidental defect, rather than general degradation.

The expanded exposure program clarified the rate of gloss loss and permitted the evaluation of a simple model of degradation. The model explains the experimental results, except yellowing, and confirms that although appearance may change considerably, the corrosion protection remains. If the degradation causes a constant loss of material due to photo-oxidation, the rates found here predict that gloss loss occurs rapidly, and that the electrochemical impedance barely changes. Thus the mechanistic description of photodegradation given here can provide a causal link between thickness loss, gloss loss and corrosion protection which can be understood and is thus more satisfactory than series of data in a correlation. In both approaches, appearance properties are not very useful warning signs for failure of barrier properties in the very thick (> 800 μm) coatings that are used to protect water pipelines. Appearance properties are dictated by the surface of a coating whereas the corrosion barrier properties are determined by the whole intact thickness.

ACKNOWLEDGEMENTS

The authors at North Dakota State University would like to thank the BASF, Carboline, Futura, LifeLast and Valspar companies for financial support and Northwest Pipe Company Inc. for coordinating the project.

REFERENCES

ASTM G173 - 03, Standard Tables for Reference Solar Spectral Irradiances: Direct Normal and Hemispherical on 37° Tilted Surface, Subcommittee: G03.99, (2012)

Bennett HE, Porteus J (1961) "Relation Between Surface Roughness and Specular Reflectance at Normal Incidence," *J. Opt. Soc. Am.*, 51(2), 123 – 129

Bourlier C, Berginc G, Saillard J (2002) "One- and Two-Dimensional Shadowing Functions for any Height and Slope Stationary Uncorrelated Surface in the Monostatic and Bistatic Configurations, IEEE Trans. Antennas Prop., 50(3), 312–324

CRC Handbook of Chemistry and Physics, 95th Edition, Haynes W. M. (ed), CRC Press, Boca Raton (2014)

Croll SG, Croes KJ, Keil BD (2015), "Electrochemical Impedance Spectroscopy: characterizing the performance of corrosion protective pipeline coatings" American Society of Civil Engineers, Pipelines Proceedings, Baltimore Maryland, August 23-26th

Croll SG, Buratto M, Calzone T, Gu C, Robinson D, Smith SM, Upadhyay V, Keil BD (2016), "Changes during Weathering of Polyurethane Water Pipeline Coatings," American Society of Civil Engineers, Pipelines Proceedings, Kansas City, Missouri, July 17 - 20th

Croll SG, Gu C, Upadhyay V, Keil BD (2017) "Polyurethane Pipeline Coatings: do Changes in Appearance Indicate Changes in Performance?," *J. Prot. Coatings and Linings*, 34(2), 30 – 42

Croll SG (2017) "Degradation of Polymer Coatings in Service: How Properties Deteriorate Due to Stochastic Damage", in Wen M., Dusek K. (eds.) Protective Coatings: Film Formation and Properties, Springer, New York.

Croll SG, Hinderliter BR (2007) "Estimating Service Lifetimes In Weathering: An Optimistic View," *J. Coat. Technol. Res.*, Vol. 4 (3), 217 – 230

Fechine GJM., Rabello MS, Souto Maior RM, Catalani, LH (2004) "Surface characterization of photodegraded poly(ethylene terephthalate). The effect of ultraviolet absorbers," *Polymer*, 45, 2303–2308