Aromatic Polyurethane Coating's Long Term Corrosion Protection Capability after Two Years of Extended Above Ground Exposure

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ABSTRACT

Steel pipelines are usually coated with aromatic polyurethane coatings to protect against corrosion by ground water. Prior to installation underground, pipeline sections may be stored on site for many months and so the coating is degraded by sunlight and its appearance suffers obvious changes. Gloss and color were monitored quantitatively during exposure to laboratory accelerated weathering for 6 months and to natural exposure in both Florida and Texas for 2 years. Prior work has shown that even after 18 months, that these appearance changes, although substantial, do not signal a significant change in corrosion protection, as assessed by electrochemical impedance spectroscopy. Concurrent chemical changes taking place in these coatings can be detected by infrared spectroscopy. Several coatings from different manufacturers were included in this study, but the nature of the chemical changes were very similar regardless of the formulation. Ultraviolet-near infrared spectroscopy showed that the increase in reflectance due to the change in color and chalking of the polyurethane coatings did not change their reflectance to solar radiation greatly and thus these changes do not protect the coating. Calculation of albedo from UV-visible-NIR spectroscopy quantifies the advantage of light colored coatings and shows that they will not heat up so much in sunlight. Regardless of color or formulation, these aromatic polyurethane coatings retain their corrosion protection because they are used in very thick layers. Surface and near surface material is degraded but the large majority of their thickness remains intact and protective. Overall, results suggest that Florida is slightly more aggressive than Texas for these coatings and so industry-standard Florida exposure would be a useful and conservative method of evaluating similar coatings. Weight change quantitatively distinguished performance between the two locations whereas other results proved very similar. This report provides the culmination of a 2 year project that demonstrates that a properly formulated and applied polyurethane coating remains suitable for its purpose even after an extended exposure period above ground produces substantial changes in appearance.

INTRODUCTION

Aromatic polyurethane coatings are chosen to protect steel water pipelines from corrosion. They are very economical and can be made to cure conveniently quickly for factory application in thicknesses that provide a substantial barrier to ground water and electrolytes. They have good mechanical toughness to resist damage during burial for service. Unfortunately, such coatings degrade readily in sunlight, so their appearance will deteriorate significantly if coated sections of pipe are stored above ground for more than a few months. Chemical reactions proceed more quickly at elevated temperatures and elevated humidity, so the degradation is worse, and more obvious, if the pipe sections are exposed in southern climates.

The effect can be seen in figure 1, where the coating on the top of the pipe has chalked, whereas the coating underneath, in shadow, retains its original appearance. Previous results on accelerated and extended natural exposures at a standard commercial weathering site in Florida [Croll et al. 2017] and a Northwest Pipe location in Texas had shown that the corrosion protection remains largely intact even though the gloss loss is complete and the color has changed considerably.

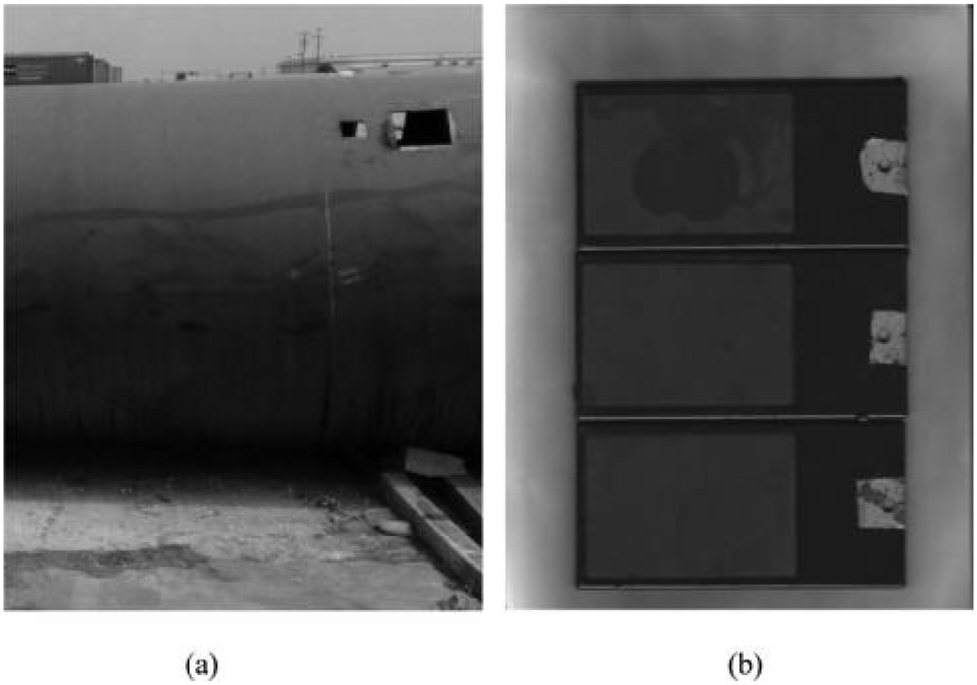

(a) (b)

Figure 1. (a) Section of coated pipe, originally dark blue, after 2years storage outside, in Texas. The exposed area on top has changed but underneath, where the coating was shielded, has not; (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.

Infrared (IR) spectroscopy is often used to provide early detection of chemical degradation and in principle can be used to monitor its progress. Ultraviolet-near infrared spectroscopy measures the absorbance or reflectance of a coating and can be used to assess whether the coating is prone to absorb damaging ultraviolet light and whether it absorbs (near-infrared, NIR) heat from sunlight so that it heats up (which would accelerate the UV degradation).

Several coatings from different manufacturers were included in this study, including some light colored coatings as well as more standard dark blue coatings. Conventional assessment by color, gloss and weight loss are given as well as the findings from IR and UV-NIR spectroscopy. This is the culmination of a 2 year project to test whether polyurethane coatings remain competent after an extended exposure period above ground.

Five coating companies contributed coatings, BASF, Carboline (RPM), Futura (ITW), LifeLast; and Valspar (Sherwin-Williams). None of the companies are identified by name in the results. A consistent color and symbol shape is used to represent data from each formulation on graphs. Many data points were generated from each of the analytical techniques and in many cases the coatings behaved very similarly. In order to limit the length of this paper, only examples are presented in some categories when all the other coatings behaved in an identical manner.

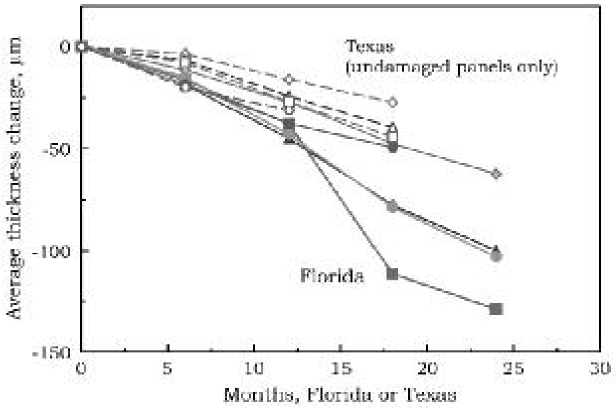


Figure 2. Thickness reduction with time, (a) Florida exposure, (b) Texas exposure. Thickness is calculated from weight loss lost/area, assuming density of 1.2 g/cc.

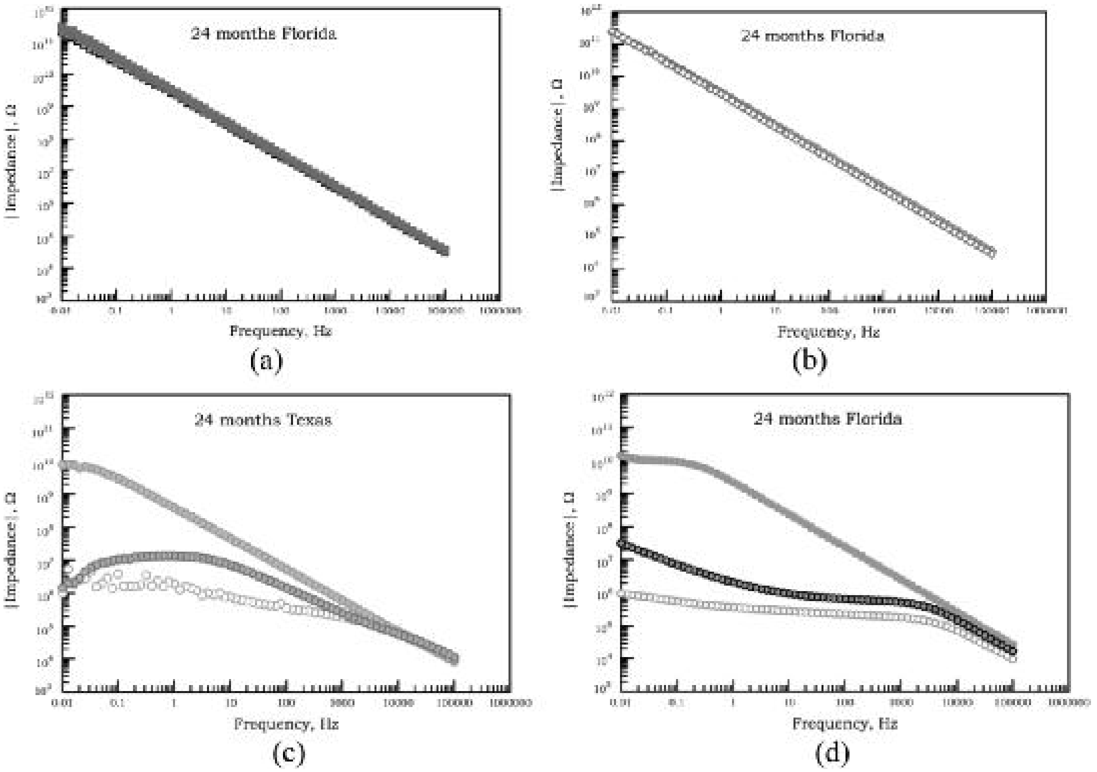


Figure 3. Electrochemical impedance before and after 24 months exposure. (a) and (b) are results from four of the five , successful coatings where the impedance is the same as its pre-exposure behavior; (c) and (d) are 24 month results from separate panels of one formulation that exhibits reduced impedance.

EXPERIMENTAL DETAILS

Color, gloss, electrochemical impedance spectroscopy (corrosion protection evaluation) and thickness reduction measurements were performed exactly as described before [Croll et al., 2016].

Most of the species to be found in organic polymers vibrate with a characteristic frequency, and thus wavelength, and can be monitored by infrared spectroscopy which uses wavelengths from 2.5 μm to 25 μm. Conventional presentation gives results are plotted with reciprocal wavelength as the independent variable (400 – 4000 cm^{-1}). The size of an absorption peak is proportional to the concentration of the species so it is possible to see whether a chemical group diminishes or increases during weathering exposure. Since the coatings to be examined are very thick, opaque and adhering well to a heavy steel substrate, spectra must be obtained from surface reflection of infrared, rather attempting to measure infrared transmission. The spectroscopy was done in "attenuated total reflectance" (Thermo Fisher Smart iTR) with a single bounce diamond crystal. The spectroscopic absorption can easily be calculated from the reflectance, but the technique only measures the infrared signature from the outer few micrometers of the material and requires that the ATR crystal is in good contact with the sample. In principle, it is possible to deduce the chemical group that corresponds to any of the peaks seen in an infrared spectrum. However, there are very many in the spectrum of a typical polymer so that was not pursued here.

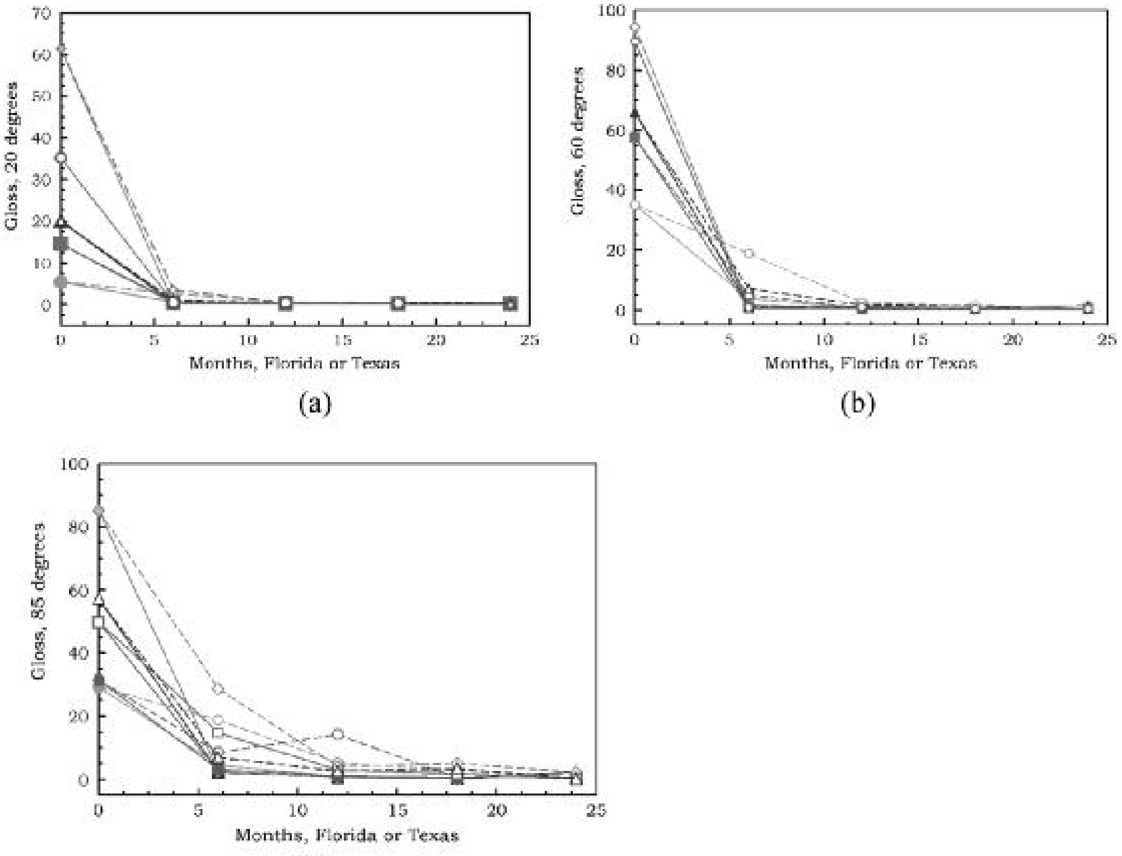
Quantitative studies of the degradation of organic polymers is often restricted to 3 easily identified regions of the spectra. Oxidation of the organic polymer during exposure leads to a greater concentration of carbonyl groups (=C=O) groups that give strong peaks around 1725 cm^{-1}. Most organic polymers have more C-H groups than anything else, so the peaks around 2850 cm^{-1} that correspond to $=CH_2$ and $-CH_3$ vibrations are a useful measure of the amount of organic polymer remaining. Hydroxyl groups (-OH) result from hydrolytic attack on the polymer, by water, so tracking the large, broad peaks that appear around 3300 cm^{-1} (also produced by –NH vibrations) provides another gauge of degradation. Other peaks might be used if one has detailed knowledge of the composition of the polymer.

Ultraviolet spectroscopy (wavelengths < 400 nm) detects the much higher energy transitions between electron energy levels that show whether a material absorbs ultraviolet radiation that may break molecular bonds. Spectroscopy in the visible region (400 – 800 nm) detects the transitions in molecular energy levels that determine color (which are otherwise translated into color coordinates). Degradation is governed by random chance and so only a few photons that are absorbed cause damage. All the other absorbed photons' energy is dissipated as heat in the material, causing an increase in temperature (that accelerates whatever damaging chemistry is occurring). Near-infrared spectroscopy (> 800 nm) detects whether a material absorbs energy in the near-infrared which contributes substantially to such heating. UV-visible-NIR results were measured in a diffuse reflectance accessory mounted in a Cary 5000 spectrometer (Agilent).

RESULTS AND DISCUSSION

Thickness Loss

Material loss due to degradation continued for the whole exposure period, see figure 2. Original coatings were at least 30 mils (800 μm) thick, so that even the greatest loss recorded here is a small fraction of the protective thickness. One free film exposed in Florida seemed to suffer unusual weight loss at 18 months, but that was probably an accidentally aggressive cleaning, since its pattern of weight loss returned to normal at 24 months. Cleaning exposure panels in a consistent way is a known problem for materials exposed to the natural environment. Panels exposed in Texas were damaged in a storm and data only extends to 18 months exposure.



(a) (b)

(c)

Figure 4. Gloss loss with exposure, (a) Gloss at 20 degrees, (b) 60 degree gloss, (c) 85 degree gloss. The results from Florida are represented by the continuous lines and filled symbols; results from Texas are shown by dashed lines and open symbols.

Thickness loss reveals that coatings exposed in Texas degrade slightly less quickly than in Florida. This is a useful differentiation which reinforces the widespread use of Florida exposure as a standard for coating durability.

Corrosion Protection

Electrochemical Impedance Spectroscopy, EIS, is a good means of testing the electrical properties of a coating film across its thickness, between a conductive, aqueous solution (usually containing a corrosive salt, sodium chloride) and the metallic substrate. High values of impedance indicate a coating film that is a good barrier to the ingress of water and salt and thus protects against corrosion.

Four of the five formulations show no significant change from the initial behavior during two years of either exposure. A common criterion of corrosion protection is that the coating should have an impedance higher than 10^9 ohm at 0.01 Hz. That is easily exceeded by most of the coatings. However, one of the formulations, (orange symbols), exposed in both Florida and Texas, shows much diminished impedance, although one of each series still exceeds 10^9 ohm. Apparently these coating suffered a problem during the sample application as the samples were independently prepared from the other 4 formulations, No panel of any formulation shows visible signs of blisters or rust appearing. The EIS detects deterioration via the electrical characteristics of the whole coating film and anything occurring underneath. Overall, it was necessary for a natural exposure to extend 18 months or more to discriminate between coatings' performance. In contrast, the accelerated laboratory testing [Croll, 2016] did not discriminate although the panels were all prepared at the same time and selected for the various exposures at random.

Gloss Loss

Initial gloss is determined by the composition of the coating and the sprayed texture. All coatings lost gloss quickly. Although material loss has continued for the whole exposure period, deterioration in the appearance of weathered coatings occurred quickly and persists at a constant, low value which does not allow further changes to be tracked.

Gloss at 85 degrees is especially affected by larger scale (> wavelength of light) features on the surface because it is near grazing incidence, so it becomes rather variable when the gloss is near zero. This is also partially true for gloss at 60 degrees.

Gloss is lost only slightly faster in Florida than in the Texas exposure. The pattern in gloss loss does not correlate with the corrosion protection results.

Color Change

The starting color depends on the pigmentation used in each formulation, but only changes in color are shown rather than absolute color. As in the case of gloss, color change occurred quickly in all cases and does not track either the continuing loss of material or the corrosion, EIS, results. With some exceptions, the degree of yellowing or overall color change is slightly less in Texas than in Florida, although the rate of change seems identical.

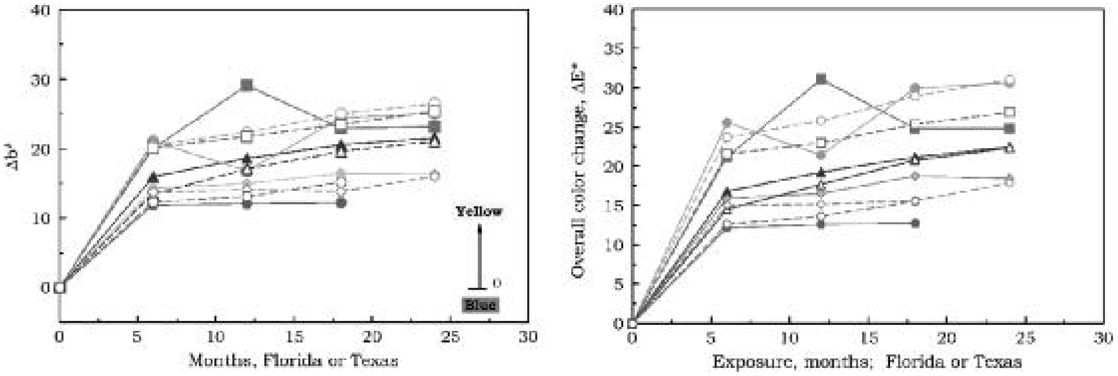


Figure 5. Color change with exposure: (a) yellowing, measured by Δb*, CIE (1976), (b) overall color change, ΔE, CIE (1976). Florida and Texas exposures (together). Results from Florida are represented by the continuous lines and filled symbols; results from Texas are shown by dashed lines and open symbols.

When fragments of material are lost after molecular degradation, any fresh material that is exposed must be quickly degraded, so the net effect is that the surface of the coating retreats towards the substrate but its appearance remains constant, after the initial changes.

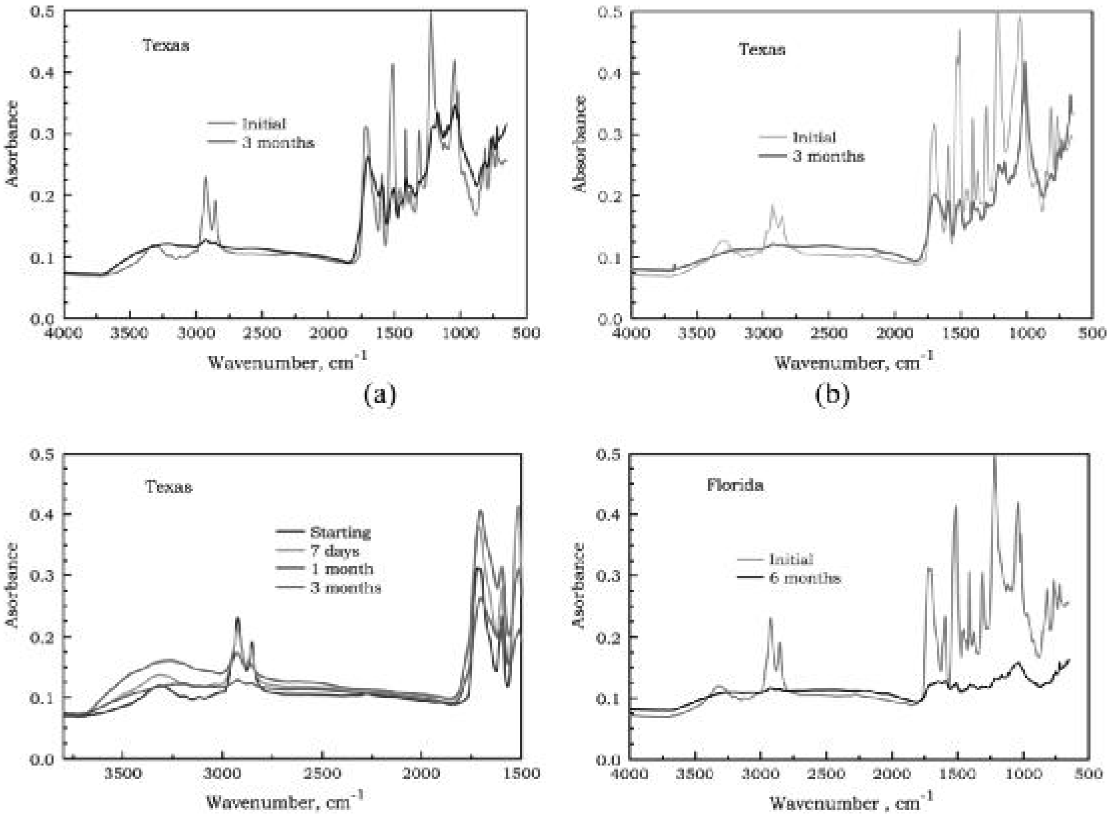


Figure 6. Infrared absorption spectra, (a) and (b) showing the complete spectra of pristine material and a weathered sample for two formulations after 3 months exposure in Texas; (c) more increments of exposure in Texas for the coating in (a) including the three regions of interest; (d) the coating in (a) exposed for 6 months in Florida.

Infrared Spectroscopy

Figure 6 shows infrared spectra from two coatings, as representative examples. These are ATR spectra that sample only the outermost few micrometers in the coating. In each case, the unweathered spectrum is shown together with a sample that has been weathered for some months. Most of the examples are from the exposures in Texas where the increments of exposure are closer together. Exposure of more than 1 month causes the spectra to become indistinct, as explained below.

One can see that there are changes in the three specific regions mentioned earlier and in the “fingerprint region” (wavenumbers less than 1500 cm^{-1}). The peaks become much less distinct as the material degrades because there is less polymer present at the surface and the surface of the coating becomes rougher and the diamond crystal of the ATR cannot make a good contact. Most of the fingerprint region becomes smoother and the peaks less distinct as the degradation progresses. It would be very difficult to use this data to deduce specific chemistry details of how each coating was degrading. One would have to scrape enough material from the surface of the coating to make a sample that could be examined via transmission spectroscopy in a pellet or a mull.

In analyzing the behavior of the three regions that depend less specifically on an individual coating's chemistry, i.e. CH, OH, and C=O regions, the peak height was measured from the top of the peak to the nearest minimum on the high wavenumber side.

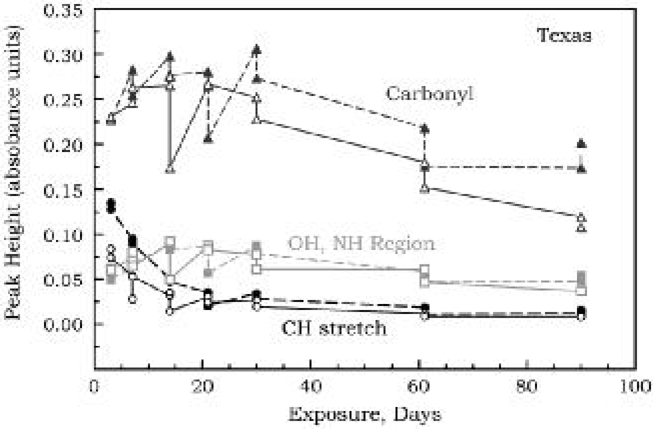


Figure 7. Quantification of trends in infrared spectra of two coating formulations exposed in Texas.

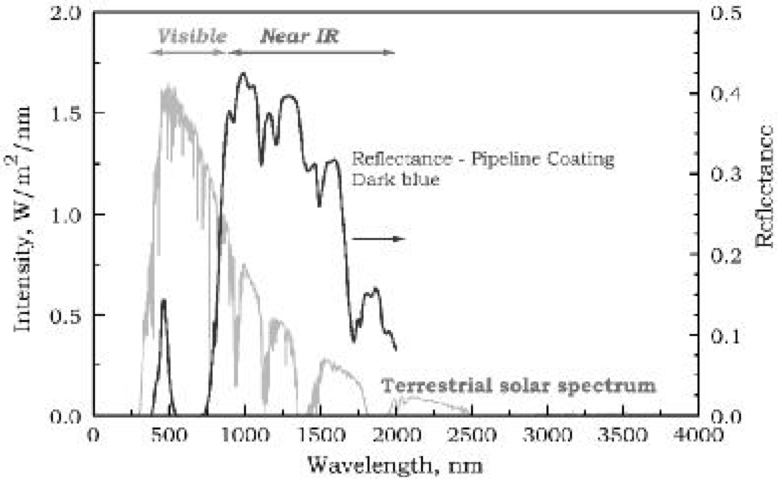


Figure 8. Solar spectrum at the Earth's surface [ASTM G173, Global Tilt] together with the reflectance spectrum of one of the dark blue coatings superimposed.

The C=O peaks increase in height and broaden for a while due to the increasing oxidation producing a variety of oxidized species on the polymer. Figure 7 shows that oxidation of the polymer as recorded by the carbonyl band increases for the first month approximately. Based on the color and gloss results, one might expect that the coating surface reaches an equilibrium in the concentration of degraded material present there but the reduction in the carbonyl band is probably because the surface of the coatings become too rough for a good spectrum to be obtained. The behavior of the OH-NH region is the same. The CH bands diminish because the amount of original polymer on the surface of the coating decreases as degradation converts that material to an oxidized (C=O) or hydrolyzed (OH) state, but as with all the other features in the spectrum, it becomes less distinct and difficult to quantify in this approach as the coating surface becomes rough.

Ultraviolet-Visible-Near Infrared Spectroscopy

Color measurements of a coating assess its reflectance spectrum, since that is the light that is returned to the observer. The solar spectrum and an example of the reflectance spectrum of a typical coating is shown in Figure 8. The coating has a peak in reflectance in the blue region of the visible spectrum with a fairly low peak amplitude, so we know that it is dark blue. It also has only a low reflectance in the near infrared spectrum so that one can expect this color to absorb solar radiation well and heat up in sunlight.

UV terrestrial radiation spans ~290 nm up to the visible spectrum. The dark blue does not reflect much light in the UV, i.e. it absorbs most of that light and thus its potentially damaging energy that could degrade the polymer because aromatic structures within the polymer absorb UV light strongly. However, most of the absorbed UV energy becomes heat like that absorbed in other spectral regions.

Figure 9 shows reflectance examples of lighter colored coatings. In each case the absorption in the visible region increases since the resin is yellowed (reflectance diminishes) and thus absorbs more light and looks darker. The spectrometer used a diffuse collector (integrating sphere) so it collects the light scattered into all directions by the increased surface roughness after degradation, so there is a small increase in reflectance at some wavelengths, but the effect is small. In fact the reflectance (and thus the absorption) changes appreciably only in the visible part of the spectrum. The yellowing is caused by the increased absorption (diminished reflection) at the blue end of the visible spectrum caused by an increase in the carbonyl content of the polymer upon oxidation. The center of the carbonyl absorption peak is at approximately 280 nm, in the UV, but the tail of the absorption peak persists into the visible part of the spectrum. It can be seen in figure 9(a), in the off-white coating, but is obscured by the blue pigment in the pale blue coating.

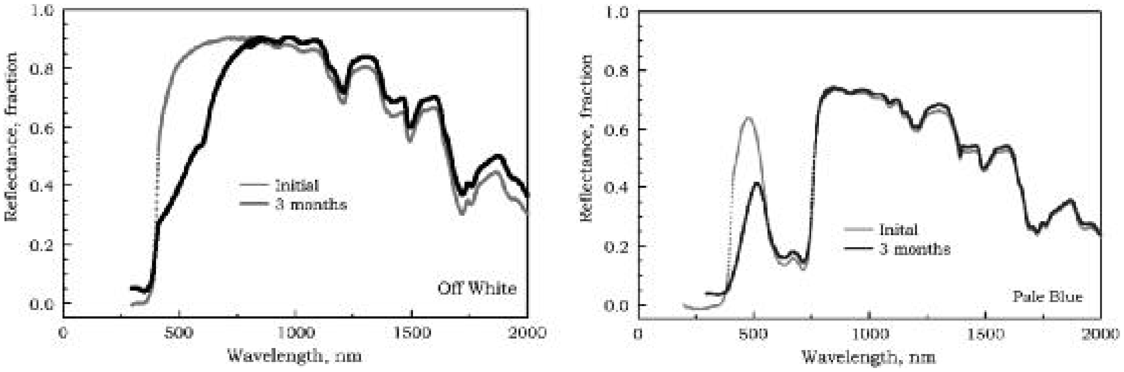


Figure 9. Change in reflectance of an (a) off-white and (b) pale blue coating before and after 3 months accelerated weathering in QUV.

The white coating does not absorb so much UV light because the white pigment is more reflective. The principal white pigment, titanium dioxide, absorbs UV wavelengths but reflects longer wavelengths and thus performs as a sunscreen for those polymers that would be susceptible to UV.

Although there is no climate data presented here, it is possible to gauge the heating effect of sunlight in a general way. Knowing the reflectance spectrum (or absorption spectrum) of a material we can calculate the fraction of light reflected or absorbed when that material is subjected to a particular illumination spectrum. Effective reflectance is calculated by integrating the reflectance spectrum, $R(\lambda)$ of a sample with the illumination spectrum, $I(\lambda)$ over the wavelengths, λ, in the illumination spectrum.

$$\text{Effective Reflectance} = \int_{\lambda_{minimum}}^{\lambda_{maximum}} R(\lambda)\, I(\lambda)\, d\lambda$$

When a surface's effective reflectance is divided by the integrated intensity of the impinging illumination it gives the fraction of the incident light that is reflected, i.e. the albedo. The fraction of radiation that is absorbed is simply (1- albedo). Figure 9 shows the albedo of various pipeline coatings and how it changes as the surface of the coating is degraded. The calculation was done using the trapezoidal method of integration in a spreadsheet using the Global Tilt Solar spectrum [ASTM G173] and the measured reflectance spectrum at 1 nm intervals.

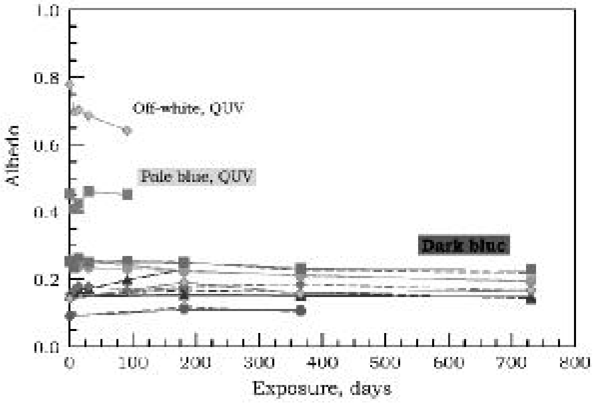


Figure 10. Albedo of pipeline coatings, and changes after exposure. Results from Florida are represented by the continuous lines and filled symbols; results from Texas are shown by dashed lines and open symbols.

The data from dark blue coatings exposed in Florida and Texas are very similar. Dark blue coatings reflect much less light than the white or pale blue coatings. In no case does the change in color or roughness due to degradation cause a major change in the albedo of a coating. Thus one can expect that the solar heating of a coated pipe is not significantly affected by degradation of the coating, which seems to be true of any of the colors tested.

Both pale colors, especially the white coating, absorb much less radiation energy than the dark blue coatings and so one could expect that they would heat up much less than a dark colored coating, as has been found [Giddings et al. 2014]. Since degradation chemistry, like all reactions, is more rapid at higher temperatures, this is another aspect of the protection afforded by light colored coatings.

SUMMARY

Gloss and color changes are dramatic and rapid for aromatic polyurethane coatings exposed in both Florida and Texas for 2 years, and in accelerated laboratory conditions for 6 months. Although no further change in appearance occurs after very brief exposure, weight loss, and thus thickness reduction continues at approximately the same rate throughout exposure, as degradation continues. Corrosion protection, measured by EIS, showed that, with one exception, corrosion protection provided by these very thick coatings remained intact with their impedance being much greater than 10^9 ohm at 0.01 Hz. Between 18 and 24 months natural exposure proved to be enough to provoke a corrosion protection failure in one coating formulation in Florida and Texas (likely due to an application problem), but not in the original accelerated testing. Its thickness loss was not indicative of unusual degradation, which supports the hypothesis that the original application may be the source of the failure.

Only weight (thickness) loss provided clear differentiation between Florida and Texas exposures. Weight loss shows that trend after comparatively brief exposure whereas EIS required almost 2 years of natural exposure to reveal a coating's weakness. That formulation did not show similar signs of failure in 6 months of accelerated laboratory exposures [Croll 2016].

Gloss loss is a loss in the reflection of visible light at a set angle and is largely determined by surface roughness. Color is the visible light returned at any or all angles and is affected by changes in light absorption caused by chemical changes due to degradation. Color becomes darker as a material changes to absorb more light, regardless of color. Color may also become lighter when a material degrades sufficiently to chalk. Infrared spectroscopy is often useful for determining what those chemical changes are exactly, so a coating chemist can adjust the formulation to provide a material that is more durable. It was impractical to prepare samples that could be used to detect changes by transmission infrared spectroscopy, but using reflectance spectroscopy also proved to have limitations when the surface of the coatings became rough and inhibited good contact between coating and the spectrometer. However, changes seen in the infrared spectra showed increased oxidation and hydrolysis, as expected but, just as in the gloss and color measurements, further changes after about one month in natural exposure were not apparent and the whole spectra became indistinct as good contact with the coating surface was lost. In addition, this form of infrared reflectance spectroscopy can only detect changes a few micrometers into the sample, so once a coating had degraded to that depth, no more changes would be seen.

Ultraviolet-near infrared spectroscopy showed that the increase in reflectance due to the change in color and chalking of the polyurethane coatings did not change their reflectance to solar radiation greatly and thus these changes do not protect the coating. UV-visible-NIR spectroscopy demonstrates why light colored coatings do not heat up so much in sunlight compared to dark blue. Light colored coatings protect themselves because the white pigment acts as a sunscreen and since they reflect overall more light, they do not get so hot and thus the degradation reactions are not so accelerated as in a dark colored coating.

None of these optical evaluations (appearance or spectroscopic methods) distinguished substantially between the Texas or Florida climate.

These polyurethane coatings retain their corrosion protection because they are used in very thick layers. Surface and near surface material is degraded and causes changes in appearance (even in the infrared) but the remainder of their thickness remains intact and protective. A properly formulated polyurethane coating remains suitable for its purpose even after 2 years of full exposure above ground.

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