

## Long Term Weathering Effects on Aromatic Polyurethane Coated Pipe

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### ABSTRACT

Polyurethane for coating of steel water pipe is used as an effective corrosion control system in the water and wastewater markets. As use has increased, questions have arisen regarding the ability of polyurethane to maintain its integrity for buried application while stored above-ground and exposed to the elements. Polyurethane used for steel water pipe will typically be specified to meet AWWA C222, which requires the use of aromatic polyurethanes that result in a resilient and flexible coating and lining system. Aromatic polyurethanes can however be susceptible to surface degradation from ultraviolet rays and can chalk or discolor when left in the sun for long periods. Historic testing in the coating industry that is related to weathering effects focuses on color changes or color shift for architectural purposes, but for buried pipe, discoloration is not a concern. Potential loss of the coating film mechanical and chemical properties due to thermal cycling above and below the glass transition temperature of the material during the exposure are of greater interest.

Testing was performed on samples of polyurethane applied to 96-inch diameter steel pipe manufactured and coated per AWWA C222 in Saginaw, Texas. Multiple test samples were removed for testing from the pipe which had been stored in Saginaw for over 24 months. The pipe was monitored over a period of time during the summer months to get an indication of the temperature fluctuations the coating was exposed to on a routine basis. Hardness and adhesion testing was performed on the coating as well. The samples were subjected to nano-indentation tests to determine any modulus shift as well as testing to determine chemical changes from the exterior of the coating to the steel surface. This paper will discuss the results of the testing of this aged polyurethane coating and discuss possible changes in the physical properties of the coating and its capability to provide its intended corrosion protection and service after 24 months in the Texas sun. Recommendations to address extended exposure of buried aromatic polyurethane coatings will also be discussed.

## INTRODUCTION

A large part of the US water supply infrastructure comprises steel water pipes. Steel pipe for carrying water is coated to protect against long term corrosion. One of the most common types of factory applied coatings is fast curing polyurethane applied on freshly grit-blasted pipe sections. These sections are then stored at the manufacturing site, then shipped to the pipeline construction site and stored again, prior to placement in the ground. Storing and shipping is done with the pipes exposed to the weather. This means that the coatings are exposed to ultraviolet radiation, heat, moisture and pollution before they fulfill their role in protecting the steel from corrosion. Pipe stored in direct sunlight can easily become too hot to touch, i.e. above 60 °C (140 °F) so any degradation chemistry that is caused by ultraviolet radiation, moisture and pollution is accelerated at this higher temperature. This cumulative exposure may last many months before the pipes are buried. An important question is whether the coatings' protective properties are significantly affected by this exposure.

Tests were conducted to determine degradation of the polyurethane coatings due to weathering. Polyurethane coatings used on buried water pipelines are made using aromatic isocyanates. They are designed to cure very quickly in thick films (> 25 mils), adhere well and remain tough and protective while buried, but are not designed to withstand extended weathering [Wypych, 1995]. In fact, these coatings commonly suffer substantial changes in color and appearance due to atmospheric weathering while they are stored.

In order to investigate the effect of UV, moisture and heat, a set of test samples of polyurethane coatings were placed in laboratory accelerated weathering exposure for 4 weeks. Another set of samples were cut in June 2013 from a 96" diameter polyurethane coated steel pipe section that had remained exposed in Texas, in hot sunlight. The pipe section has remained stored in the open, since July 2011. Figure 1 shows that temperature sensors placed on the pipe indicated that some parts of the pipes reached 145 °F (63 °C).

The temperature sensors were placed on the pipe in July of 2013 and recorded temperatures for a month. Ambient temperature, humidity (see Figure 2), radiation and UV data was also gathered during the same period. The temperature probes were located at the 10, 2 and 6 o'clock positions on the pipe. The pipe ends were sitting in a North to South orientation. The full details of the data gathered can be found in *Exposure: Polyurethane Coating Response To Cyclic Heat Load And Ultraviolet Impact In The Texas Environment*, [Giddings, 2014].

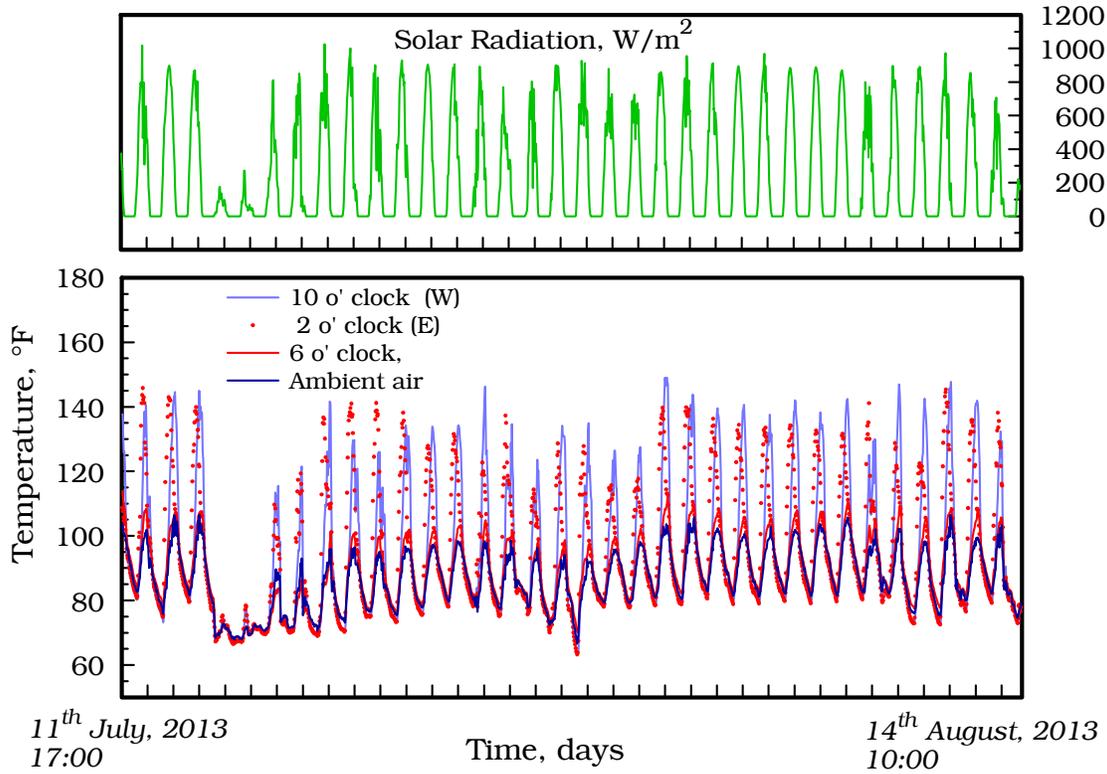


Figure 1. Pipe temperature, and Solar radiation, Saginaw Texas, July to August 2013

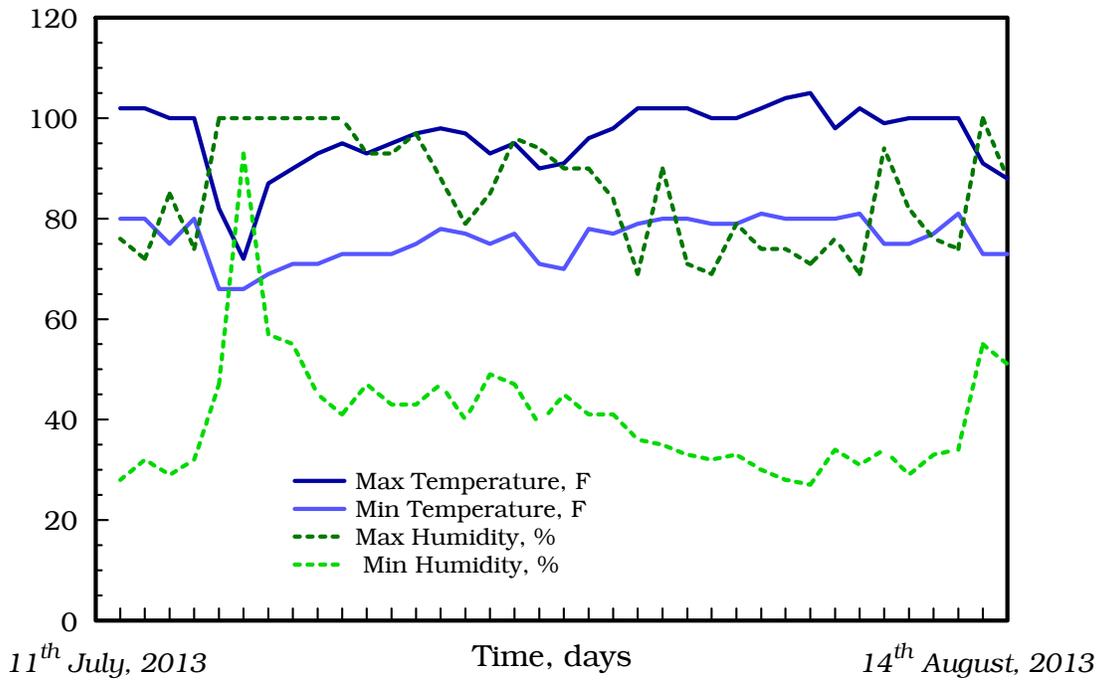


Figure 2. Ambient temperature and humidity readings from neighboring Meacham International Airport, in Fort Worth

The coatings on the 96" pipe had discolored and lost gloss during their lengthy exposure and there is a concern that after this kind and length of exposure, they may no longer provide the required long-term corrosion protection after burial.

To test the coating, six coupons were removed for testing.

Sample numbers:

*Cement lined pipe:*

- #1: East side of pipe at 10 o'clock
- #2: West side of pipe at 2 o'clock
- #3: Bottom of pipe at 6 o'clock (north end)

*Pipe without cement lining:*

- #4: West side of pipe at 10 o'clock
- #5: East side at 2 o'clock
- #6: Bottom of pipe at 6 o'clock (south end)

From each of the coupons, polished cross-sections of urethane coatings on steel pipe were prepared by Northwest Pipe and sent to North Dakota State University (NDSU), Department of Coatings and Polymeric Materials for evaluation. The objective was to examine how the properties of the coating change from the outer exposed surface to the steel substrate. The evaluation comprised measurement of the mechanical properties through the thickness of the coating, molecular spectroscopy (infrared) and scanning electron microscopy to assess the depth of chemical degradation.

Also from the coupons, square coated sections were cut to be evaluated for their corrosion protection. These sections were studied for one month using electrochemical impedance spectroscopy on areas of the coating that were continuously immersed in salt solution.

All the coating samples from the top of the pipe (10 and 2 o'clock) had degraded and became darker because the originally blue coating had become more yellow. The samples from underneath (6 o'clock) remained at their original color. Yellowing is typical of polyurethane coatings, especially those that use aromatic isocyanates in order to achieve rapid curing. Yellowing often occurs quickly and before any cracking occurs.

In this testing, sample 1 was chosen to represent the degraded material and was compared against sample 3, which represented the coating with less exposure to direct UV energy and smaller amplitude temperature changes.

### Mechanical Properties

Nanoindentation measurements were done on the polished cross-section of the coatings using a Hysitron Triboindenter®. They showed that the tensile (Young's) modulus through the depth of the coatings (6 samples) remained at levels typical of intact coatings, see Figure 3, except close (within 100 microns) to the outer surface. The modulus at the very outer edge was difficult to measure because locating the nanoindenter tip at a precise distance from the coating surface could not be achieved and the polished surface was not so smooth near the outer surface. However, attempted measurements indicate that there is a reduction in modulus within 50 micron (2 mil), to around 1 GPa (giga pascal) or less.

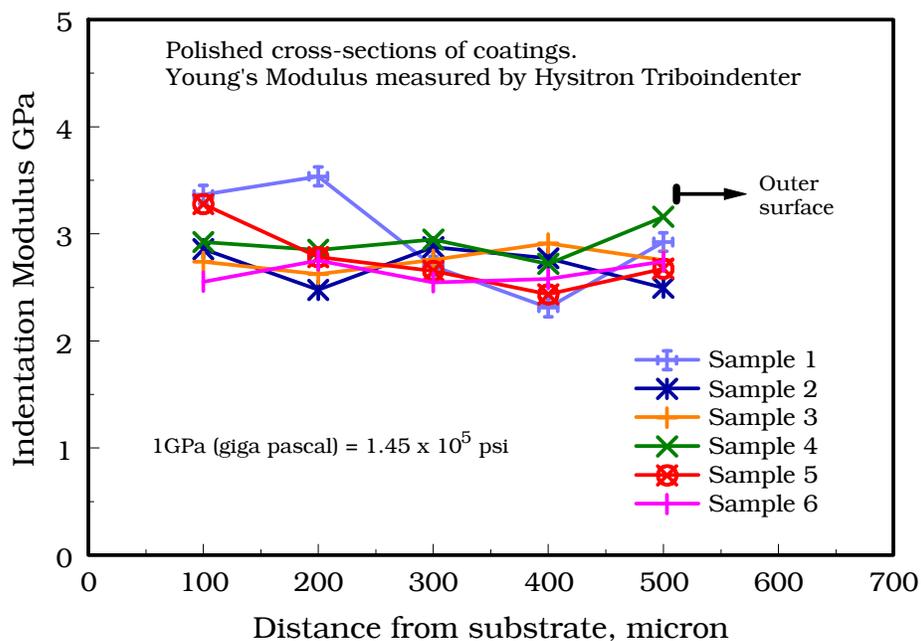


Figure 3. Nanoindentation results for modulus through thickness of coating.

### Chemistry of Degradation

The top surface of the coating was compared to the inner material using infrared spectroscopy. First the outer, discolored material was carefully shaved from the coating and cryogenically ground into a powder. This was made into a pellet with potassium bromide which could be examined in normal transmission mode spectroscopy. A similar procedure examined interior material. Sample 1 (degraded) was compared to sample 3.

The result of the spectroscopic examination was that both samples show a slightly different spectrum near the surface than in the depth of the coating. This is typical of coatings, since the more surface active species in the mixture will tend to remain at the interface with air (like surfactants) and the curing of a coating near the surface will be different because the curing exotherm cannot raise the temperature as much. Both

spectra from sample 1 are very similar to spectra from sample 3, and show no signs of significant change.

### Scanning Electron Microscopy

Again, only samples 3 and 1 were examined. They were coated with carbon and examined in the scanning electron microscope at NDSU. There is a length scale bar (micrometers,  $\mu\text{m}$ ) at the bottom of each image that shows the effective magnification. 1 mil = 25.4  $\mu\text{m}$ . Samples 1 and 3 are very similar. There is little evidence of significant degradation in these images, except within 5-10  $\mu\text{m}$  (micrometers) of the surface of the coating.

Sample 1 (degraded sample) views are found in Figures 4 - 7.

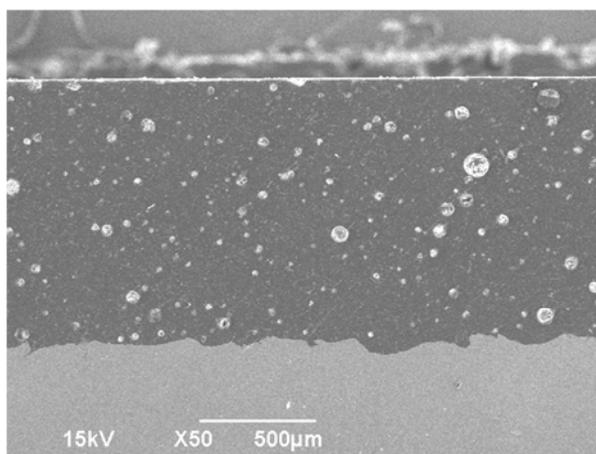


Figure 4. Degraded sample #1 from near pipe summit. General view of entire coating thickness, from steel (bottom) to outer surface

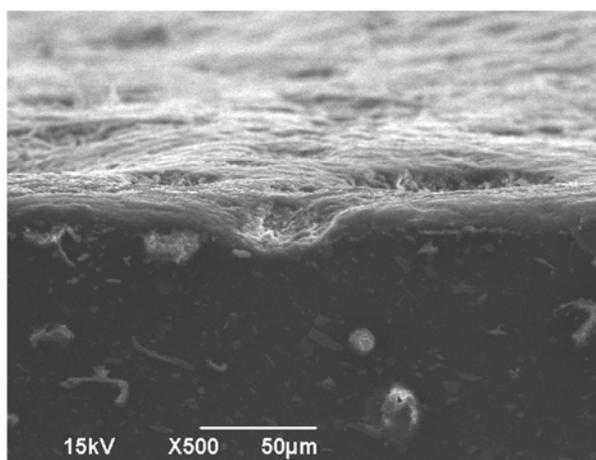


Figure 5. Degraded sample #1, higher magnification of outer surface

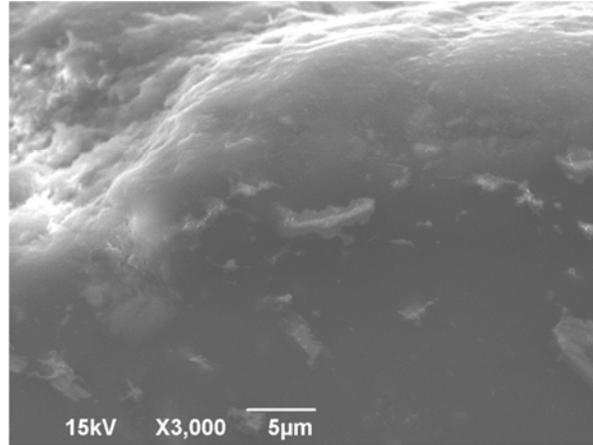


Figure 6. Degraded sample #1, outer surface

Figure 6 shows that there is a layer approximately 5-10  $\mu\text{m}$  deep at the outer surface that is slightly different and may represent the depth of degradation into the coating. However, it is not uncommon for coatings to have different, more surface active composition near the interface with air (see comment above).

Sample 3 was taken from underneath the pipe and was thus protected from sunlight and seemed to retain the original color of the coating, views are found in Figures 7 through 9.

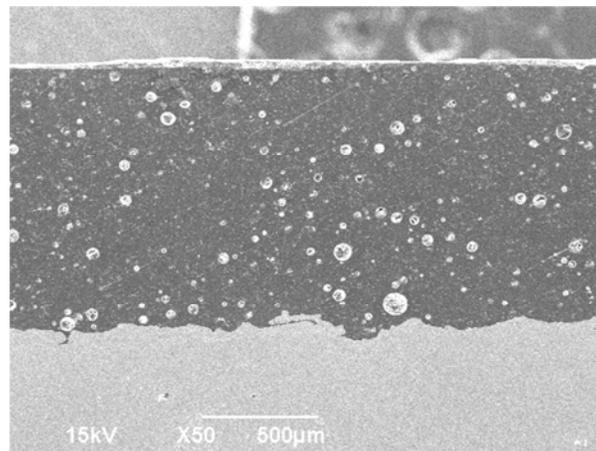


Figure 7. Protected sample #3 from shaded pipe bottom. General view of entire coating thickness, from steel (bottom) to outer surface

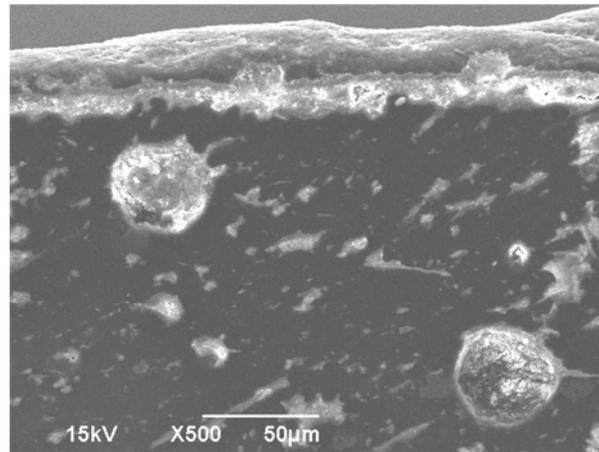


Figure 8. Protected sample #3, higher magnification of outer surface

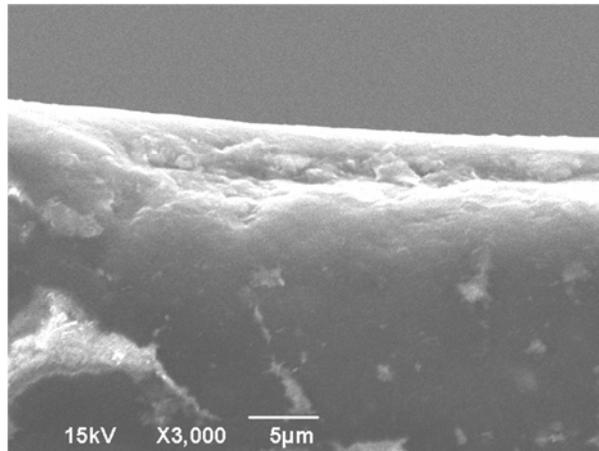


Figure 9. Protected sample #1, outer surface

No significant failure of the coatings was been detected by any of the techniques used. None of mechanical modulus, infrared spectroscopy, nor scanning electron microscopy showed any change beyond the very outer skin of the coating.

It appears that the outer yellowed appearance corresponds to damage that is most sensitively seen in electron microscopy and appears to extend 5 – 10 µm into the coating from the outer surface.

### **LABORATORY ACCELERATED WEATHERING**

In this study, the tensile adhesion test was used to monitor the mechanical performance of the coatings and color and gloss measurements were used to evaluate how readily the coating composition degraded in the laboratory exposure conditions.

### Experimental Details

Polyurethane coatings were applied according to their manufacturers' requirements and the American Water Works Association (AWWA) standard C222 on steel panels. AWWA C222 requires a minimum surface cleanliness of SSPC SP 10 'near white' blast but the panel preparation exceeded that and was done to SSPC SP5 'white' metal blast. The measured surface profile exceeded the AWWA C222 65  $\mu\text{m}$  (2.5 mil) requirement. Coating thicknesses were all measured and typically greater than 760  $\mu\text{m}$  (30 mils). Free films of each of the coating systems were prepared by spraying onto smoothed polyethylene sheet.

The exposures and coating tests were carried out at NDSU. The accelerated exposure chosen was according to ASTM G154 in a QUV<sup>®</sup> chamber (Q-Lab Company) using a 340A fluorescent light source. The exposure cycle uses 8 hours of ultraviolet, UV, irradiation of 1.55  $\text{W}/\text{m}^2/\text{nm}$ , at 60 °C followed by 4 hours of water condensation without irradiation, at 50 °C. Panels of the coating were subjected to either 1 week of this exposure, or 4 weeks. Significant color change was observed after 4 weeks for the coatings. This accelerated weathering cycle is used to evaluate coatings on metal parts in other industries.

In order to determine whether temperature alone would cause significant change to the coatings, panels that were otherwise unexposed were kept in a laboratory oven at 60 °C, for 1 week or 4 weeks. Each of the coating samples were evaluated after each exposure condition. In all cases, the panels were removed from the exposure and allowed to equilibrate under normal laboratory conditions for 2 weeks before any testing. In this way, their moisture content would stabilize to a value representative of normal laboratory conditions.

Gloss measurements were done using a Novo-Gloss TRIO<sup>™</sup> from Rhopoint Instruments at 20°, 60° and 85°. Gloss results are a relative value compared to the reflectance of a standard, very smooth black glass. Thus 100% gloss means that the surface reflects as much light as does the glass, at that angle. Color measurements were recorded in the L\* a\* b\* system using X-Rite SP60 Series sphere spectrophotometer using D65 (Commission Internationale de l'Éclairage, CIE) illumination with a 10° acceptance angle.

Thermal analysis was done on the samples of the free films in order to measure the effect of elevated temperature, especially in the oven and accelerated weathering. Differential scanning calorimetry (DSC) was performed using a 5 °C/minute heat-cool-heat cycle under a nitrogen atmosphere in an aluminum pan with a lid. Weight loss with increasing temperature (thermogravimetric analysis, TGA) was done as the temperature increased at 5 °C/minute. Mechanical properties were measured dynamically in tension at 1 Hz as the temperature increased at 3 °C/minute (dynamic mechanical thermal analysis, DMTA).

Tensile pull off tests were done using a PATTI<sup>®</sup> Quantum adhesion tester from M.E. Taylor Engineering, with an F-20 (5¾" overall diameter) piston. This conforms to ASTM 4541, test method D, type IV. The 2-component epoxy adhesive used to glue the stubs to the coatings was Scotchweld<sup>®</sup> DP460 from 3M.

Prior to application of the adhesion dolly, the coating was sanded with a clean, coarse 'Dual Angle Sanding Sponge' (3M) in a circular pattern to roughen the surface and to remove the texture that had remained after coating application. In the case of the panels that had degraded and had changed appearance, the preliminary sanding was continued until the color of the unexposed material was revealed again. No tensile tests were done until the adhesive had cured for at least 7 days at room temperature. Tensile failures between adhesive and coating were more common if the curing period for the adhesive was significantly shorter.

### Results and Discussion

In all cases the appearance of these coatings changed when exposed to accelerated weathering. Accelerated weathering necessarily stresses materials differently to natural weathering conditions since the objective is to provide results quickly. Although these methods are unreliable in providing correlations with performance in natural exposure [Martin et al., 2005] they do demonstrate whether a coating is especially susceptible to ultraviolet radiation, or moisture etc. or displays another particular weakness. None of the coatings tested here showed unexpected susceptibility to the accelerated exposure.

#### *Gloss*

Gloss diminished when the coating was subjected to ultraviolet for 4 weeks, but less when the exposure was only an increase in temperature to 60 °C.

These coatings suffered a visible reduction in gloss when exposed to ultraviolet radiation. Gloss is the mirror-like reflection from the surface of a material. It is a measurement taken over an area of some square millimeters so sub-surface reflections can contribute to the reflectance, but only from a depth to which light can penetrate and return. In pigmented coatings, this depth will only be a very small fraction (perhaps 1-2 mils), depending on pigmentation, of the thickness of these pipeline coatings and cannot be characteristic of the material near the steel substrate.

#### *Color*

Changes in color are due to changes in light absorption due to chemical changes in the composition of the coating ingredients. If a coating becomes more colored by virtue of these changes, it often becomes darker so that changes are seen in the lightness, L\*, as well as in the co-ordinates that represent color. However, it is possible for the surface scattering due to a much roughened surface to diminish somewhat the effect. These coatings follow normal trends and yellow significantly when exposed to the accelerated weathering including radiation.

Coatings degrade thermally, often with many of the same chemical changes that occur under irradiation, and color measurement has detected changes in these coatings that have suffered only moderate heat.

Color measurements determine only the outward appearance of a coating. For comparison, decorative paints, e.g. reasonable quality housepaint with typical pigmentation, achieve their full color or opacity when they are approximately 50  $\mu\text{m}$  (2 mils) thick. These pipeline coatings are very thick so the color measurements cannot indicate what happens closer to the substrate. However, they are sensitive and do indicate that degradation occurs and can be used to assess the relative degradation rates between coatings.

*Tensile Pull-Off Failure Stress*

The tensile pull-off (adhesion) failure stress was very high for the unexposed, un-aged coatings, see Table 1. In all cases the first week of oven aging produced a small reduction in failure stress but after 4 weeks oven aging the failure stress actually exceeded the value for the pristine coating. The results for the coatings subjected to accelerated weathering are a little lower than for the unexposed coatings, but still achieve very high values. All the exposed coatings were sanded down to material that had the same color as the original material (when sanded) so the dollies were glued to material that was apparently unaffected.

Table 1. Tensile Pull-off Stress Values

Unexposed	60 °C, 1 week	60 °C, 4 weeks	Accelerated Weathering, 1 week	Accelerated Weathering, 4 weeks
5130 psi (920 MPa)	4880 psi (210 MPa)	5230 psi (470 MPa)	4760 psi (450 MPa)	4940 psi (370 MPa)

Changes to gloss and color were minor after oven aging which indicates that any damage was very minor.

Accelerated weathering exposure is different from oven aging in two obvious ways. There is ultraviolet radiation and condensing humidity. Not only will the coatings be damaged, from the exterior, by the radiation, but water will permeate the coatings. Water will swell them, plasticize them, possibly cause chemical changes and may leach material out. Thus there are many more possibilities for change to the coatings. It is obvious that the coatings suffered external damage because both the gloss and color changed substantially. In all cases the pull-off failure stress was reduced somewhat (10% or less) from the value obtained on the unexposed coating. Tests were done on places where the coating was abraded down to material that visually appeared to be the same color as the unexposed coating, so obviously degraded material was excluded.

In an absolute sense, the tensile failure stresses remained very high so the coatings remain very competent, as determined by the tensile test. None of the metal areas exposed appeared to be corroded or otherwise changed when the coating was pulled off so the coatings have fulfilled their protective role in this exposure series.

The standard deviation in the results was typically 10% of the mean for any set of circumstances. Although a great deal of care was taken in doing the adhesion test, failure modes changed from place to place on the 12 x 6 inch panels, even if the values recorded for the failure stress showed no corresponding variation. Tests performed several days apart showed a similar failure mode and failure value to results gained from neighboring locations.

## CONCLUSIONS

It can be seen in both series of tests that polyurethane coatings used on steel pipe will have degradation on the surface that is limited to a thin layer near the surface when exposed to weathering, which is expected with this type of aromatic polyurethane composition. The tests show the degradation to be limited to a thin layer relative to the overall film thickness (>25 mils) and the coating below appears to be unaffected by the exposure. The coating material under the degraded material in the tested samples would be expected to perform as intended.

No failure of the coatings exposed to natural weathering in Texas was been detected by any of the techniques used. None of mechanical modulus, infrared spectroscopy, nor scanning electron microscopy showed any change beyond the very outer skin of the coating. The outer yellowed appearance corresponds was most sensitively seen in electron microscopy and appears to extend 5 – 10  $\mu\text{m}$  into the coating from the outer surface.

Pull-off adhesion testing was done on coatings exposed to laboratory accelerated weathering. Tests performed several days apart showed a similar failure mode and failure value to results gained from neighboring locations. If, as hoped, the preparation of the adhesion test was not responsible for the variations, then there are other variables that influence the failure mode.

Although the coatings were sanded down to a level where they appeared not to be degraded, the accelerated weathering produced failure stresses that were a little lower than the best for each coating. Nevertheless, all the values in this study are very high compared to expectations for polyurethane coatings on steel pipelines. None of the metal areas exposed appeared to be corroded or otherwise changed when the coating was pulled off so the coatings have fulfilled their protective role in this exposure series. The outer surface of these coatings degrades when exposed to ultraviolet radiation, as detected by gloss and color changes, but the exposures here were comparatively brief and not done in a natural environment. A more extended exposure series might lead to a greater reduction in failure stress.

These coatings are very thick which is important since the expectation is that a substantial un-degraded thickness must remain as a protective barrier. Unfortunately, the ablation rate is not known for these coatings, neither is the degradation rate in terms of chemical changes. It is well known that degraded polymers become more brittle and less competent barriers to moisture and other species [Wypych, 1995]. Depending on the exposure, tensile failure stress determined in the factory just after coating application may not be representative of the value as it goes in the ground. In addition, this pull-off adhesion testing would not be predictive of pipeline performance since there is no quantified relationship between coating adhesion and their long term protection against corrosion [Forsgren, 2006].

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