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Stainless Steel Corrosion Studies

Final Report: FY17 End of-Year

Test Substances: MEK (methyl ethyl ketone), Neoprene (polychloroprene)

Test Substrates: Stainless Steel 304L

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SUMMARY

Two materials are being considered in applications requiring their contact against stainless steel surfaces. These materials include the solvent methyl ethyl ketone (MEK), and the polymer neoprene (polychloroprene). There is concern that contact of these materials with stainless steel substrates may lead to corrosion. To address these concerns we have undertaken corrosion studies under conditions expected to be more aggressive than in intended applications. These conditions include elevated temperature and humidity, and submersion and suspension in solvent vapors, in an attempt to accelerate any potential deleterious interactions. Corrosion rates below 0.1 mpy have historically been deemed INSIGNIFICANT from a WR *Production* standpoint; corresponding guidelines for non-production applications are lacking. A summary of our current work indicates:

- there is no evidence of corrosion of stainless steel submerged in MEK, or suspended in MEK vapor, at 50 °C, over ~ 34 months. Corrosion rates are below 0.1 mpy. The MEK develops a yellow tint over time, but this is not caused by interaction with the stainless steel substrate. Fourier Transform Infrared (FTIR) transmission and FTIR-Attenuated Total Reflection (ATR) of the aged MEK show no significant chemical alteration of the solvent.
- there is no evidence of corrosion of stainless steel held in tight contact with neoprene at 50 °C and high humidity. Originally, aluminum brackets were used to hold stainless steel coupons to neoprene. The aluminum brackets and the neoprene they contacted showed degradation within the first two months of the study. The brackets were changed to sacrificial steel coupons, and the degraded neoprene was replaced, and the experiment continued. The neoprene is showing minor changes over time by FTIR-ATR.

CORROSION TEST CONDITIONS

MEK Studies

Studies involving MEK and stainless steel substrates used metal coupons that were submerged, and coupons suspended in MEK vapor; both conditions were held at 50 ^{o}C. The substrates were periodically visually inspected and weighed.

Neoprene Studies

Studies with neoprene and stainless steel coupons pressed together were held 50 ^{o}C and high humidity. Witness substrates not in contact with neoprene were held under identical environmental conditions.

EXPERIMENTAL DETAILS

Gravimetric corrosion studies were performed using guidance provided in corrosion testing standards ASTM G31-72, ASTM G1-03, and NACE TM0169-2000. Stainless steel substrates were cleaned by sonication in 10% nitric acid at 50 ^{o}C. After cleaning substrates were dried, photographed, and weighed. All stainless steel coupons were visually inspected and photographed prior to corrosion testing, and at selected intervals during corrosion testing. During testing, substrates were held in sealed containers at elevated temperature inside air-filled ovens. Substrate weights were measured with a Mettler AG204 or Sartorius A120S balance which were checked periodically with calibrated weights. Substrate dimensions were measured using a micrometer. Stainless steel 304L corrosion substrates (3 x 0.5 inch, ~ 70 mils thick; ~ 10 grams for SS; engraved with unique identifiers) were procured through Alabama Specialty Products Inc. MEK was supplied by Fisher Scientific. Neoprene was procured from Chesapeake Bay Rubber Company. Fisher Scientific trace metal nitric acid was used to clean (etch) the stainless steel corrosion substrates. Deionized water from a Nanopure system (resistivity ≥ 18 MΩ-cm) was used for coupon rinsing and in the preparation of the 10% nitric acid used for substrate cleaning.

XPS is a surface-sensitive analytical technique used to determine the elemental composition and chemical valence at the top ~ 5 nm of solid materials and is particularly well suited for investigating corrosion layer formation, composition, and thickness on stainless steels[1,2]. Stainless steels are corrosion resistant due to the formation of a passive chromium oxide layer over the top~ 5 nm of surface. XPS analysis combined with ion sputtering to ablate material from a substrate surface is routinely used in corrosion studies to probe the chemical composition of metal surfaces as a function of depth into the substrate (depth profiling). Changes in the thickness of oxide layers, and the concentration and valence state of iron, chromium, or corrosive species as a function of penetration into the surface enable one to determine corrosion effects and mechanisms. XPS data were collected using a Physical Electronics VersaProbe II system with a base pressure below 1×10^{-7} Pa. A variable-size, monochromated Al k-alpha x-ray source (1487 eV) was used and photoelectrons were energy sorted using a hemispherical analyzer. Samples were at room temperature. XP spectra are reported in terms of binding energy (BE) and instrument calibration was performed in accordance with ASTM procedure. Elemental composition was determined using survey scans at a pass energy of 117 eV. A pass energy of 29 eV was used for high-resolution scans to determine chemical valence state. Depth profiling by ion sputtering was carried out using 2 kV argon ions. Charge neutralization for insulating samples is accomplished by focusing low energy ions and electrons at the spot of x-ray impingement.

Transmission-FTIR is a sampling technique where a liquid or a thin slice of semi-translucent material is placed in the path of an IR beam. Attenuated Total Reflection - Fourier Transform Infrared (ATR-FTIR) is an infrared vibrational spectroscopy in which light is passed through a crystal to develop an evanescent wave which spills into a sample in contact with the crystal. ATR-FTIR is particularly well suited to probing solid materials. ATR-FTIR measurements were collected using a Nicolet 6700 FTIR with a Smart OMNI-Sampler™ Germanium ATR sampling accessory that uses a single-reflection horizontal Germanium ATR crystal that has a spectral range of 4000 to 675 cm^{-1}. Transmission samples were tested on the same equipment using a transmission plate accessory and Thermo Scientific transmission sample holder. Background spectral scans were taken periodically during testing to ensure that the spectrum of the sample did not deviate.

GRAVIMETRIC CORROSION RATES

Corrosion rates, expressed as a dimensional change of the stainless substrate in mils-per-year (mpy), were calculated using the formula

$$\mathbf{R} = (K * \Delta W) / (A * t * \rho)$$

where ΔW is the change in substrate weight (grams)

A is substrate area (cm^2)

t is time (hours)

ρ is substrate density (g/cc)

K is a conversion factor ($3.45x10^6$) to provide corrosion rate in mpy when the units for ΔW, A, t, and ρ are as noted.

The density of stainless steel was taken as 8.0 g/cm^2.

In most studies we view and weigh coupons periodically, often without substrate cleaning (leaving any corrosion product intact). We anticipate any corrosion under these circumstances would be shown as a weight gain for an adherent corrosion layer. Weight changes are determined and an effective ΔW is calculated assuming that the weight gain is due to the formation of metal oxides. The benefit of this method is the ability to use a single substrate for multiple measurements over time; *e.g.*, a substrate used for a one-month measurement is returned to experimental conditions and can provide a two-month measurement later. As studies progress we also clean corrosion products from the substrates when corrosion is readily observable or at designated time intervals (even if corrosion is not readily observable). For the submersion corrosion testing the weight of stainless steel substrates was always determined after cleaning the substrates to remove any corrosion product. This cleaning by sonication and acid etching results in a weight loss for the substrate if corrosion products have been formed and removed. This method can provide a more precise determination of ***R***, since the weight of stainless removed is greater than the weight of oxygen added (for a given amount of corrosion). The drawback to this method is that *time zero* must start over each time the substrate is cleaned.

MEK SOLVENT CORROSION STUDIES

Methyl ethyl ketone (1-butanone) is often used as a degreasing and cleaning agent for surfaces. MEK is a polar, aprotic, general purpose organic solvent, which is typically stored in glass and steel containers. As noted in the ExxonMobil™ MEK Product Material Safety Data Sheet, stainless steel is considered a suitable material for MEK storage[3].

The MEK used in the corrosion study developed a yellow tint after nine months at elevated temperature. The MEK liquid in the submersion study as well as the MEK liquid sample without stainless steel contact both exhibited approximately the same degree of yellowing. MEK liquid used in the vapor study condensed in its container and the residue was a sticky yellowish substance. Colloquial lore indicates MEK can exhibit a translucent yellow tint as it ages. Figure 8 shows FTIR spectra of aged and as-received MEK. There is no chemical degradation of the MEK regardless of the yellow tint that is observed. [The negative peak at ~ 2350 cm^{-1} in the aged MEK sample of Figure 6 arises from ambient CO_2.] Figure 7 shows a photo of aged and as-received MEK.

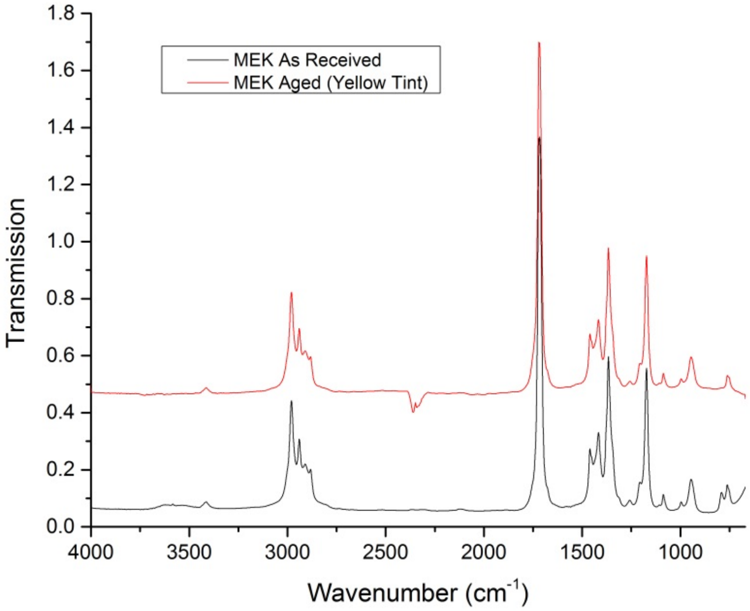

Figure 6: FT-IR of MEK as-received from the vendor vs. MEK that has been aged in contact with stainless steel at elevated temperature.

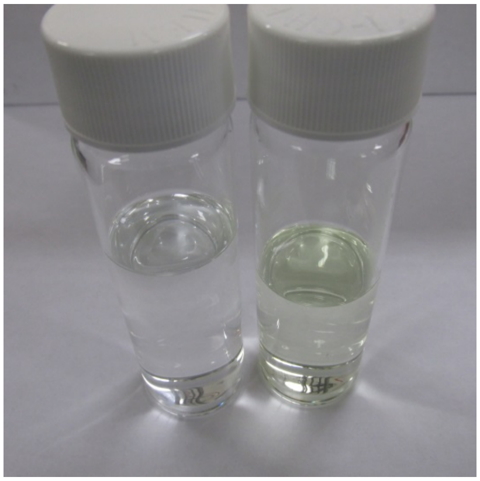

Figure 7: As-received MEK (left) and aged MEK after ~ 1 year contact with stainless steel at elevated temperature (right).

Figure 8 shows stainless steel substrates before exposure and after submersion exposure to MEK. No corrosion is visually observed on any stainless steel substrates exposed to MEK. In the submersion study all substrates appeared clean during submersion. Substrates removed from MEK appeared to have a slight dullness after drying. In the vapor study the substrates removed from the MEK vapor appeared to have a dull surface or film after drying. This surface dullness and film are not observed in the absence of solvent exposure. We believe the film to be residue of dried solvent. This residue can removed by wiping the substrate with a Kimwipe wetted with alcohol. The residue and underlying substrate surface were analyzed by XPS and no anomalies were found.

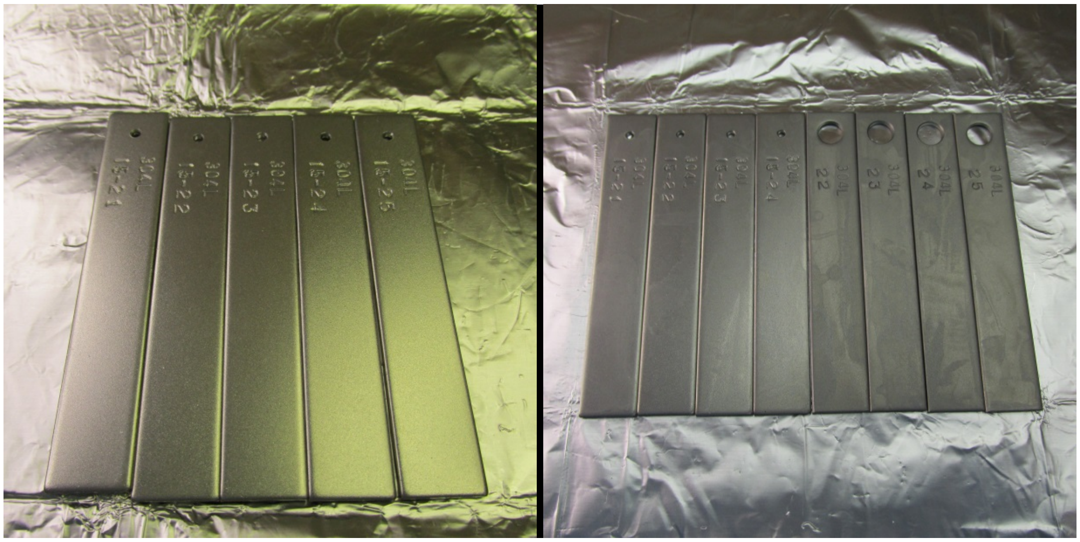

Figure 8: Stainless steel coupons before and during corrosion testing. Left: initial stainless steel coupons. Right: MEK vapor exposure ~ 107 days.

Figure 9 shows the corrosion rate (mpy) of stainless steel exposed to a MEK vapor and stainless steel submerged in MEK. Arrows indicate corrosion rates on substrates that have undergone 'final' cleaning (acid etching). Corrosion rates are well below 0.1 mpy, and are almost always within the error bars imposed by the uncertainty in the substrate weight measurement (0.3 mg). Corrosion rates are effectively zero over the course of this study.

Residue drying on substrate surfaces can lead to slight increases in substrate weight (translated as negative corrosion rates in the figures). In cases where stainless steel substrates underwent final cleaning (acid etching) corrosion rates were generally closer to zero than for uncleaned substrates, indicative of the removal of residue but no underlying substrate corrosion. This is denoted in Figure 9 with arrows indicating where selected substrates have been acid cleaned. At the end of 34 months the last of the stainless steel samples were 'final' cleaned and the results indicate no sign of significant corrosion for either the vapor exposed or the submerged samples for the full duration of the study.

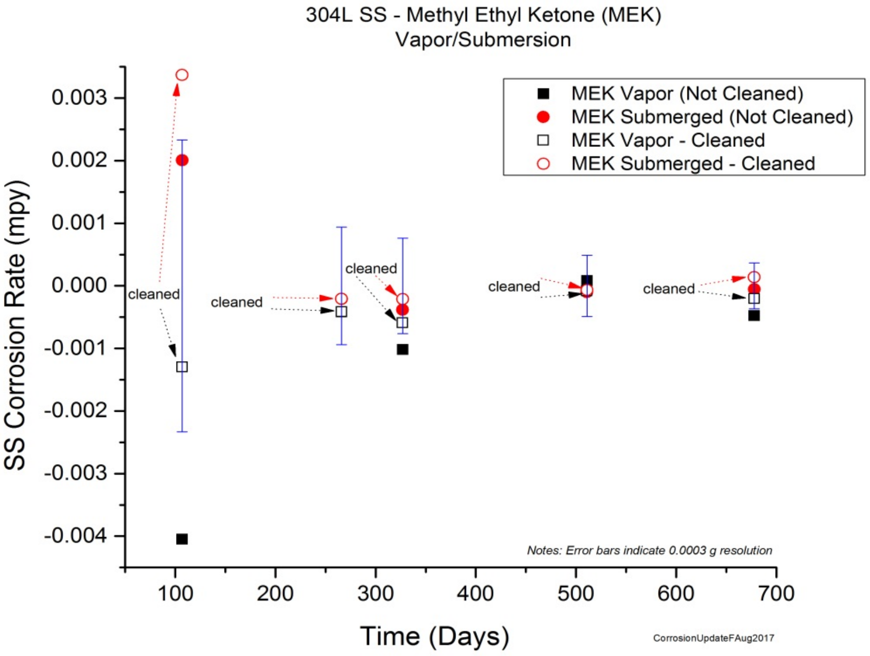

Figure 9: Corrosion rate (mpy) for stainless steel substrates submerged in MEK and exposed to MEK vapor, at 50 °C. Error bars represent the uncertainty of the corrosion rate based on an uncertainty of 0.3 *mg* in the substrate weight.

Figure 10 shows stainless steel coupons in the vapor chamber sitting in a stainless steel wire mesh tray hanging above a beaker of MEK.

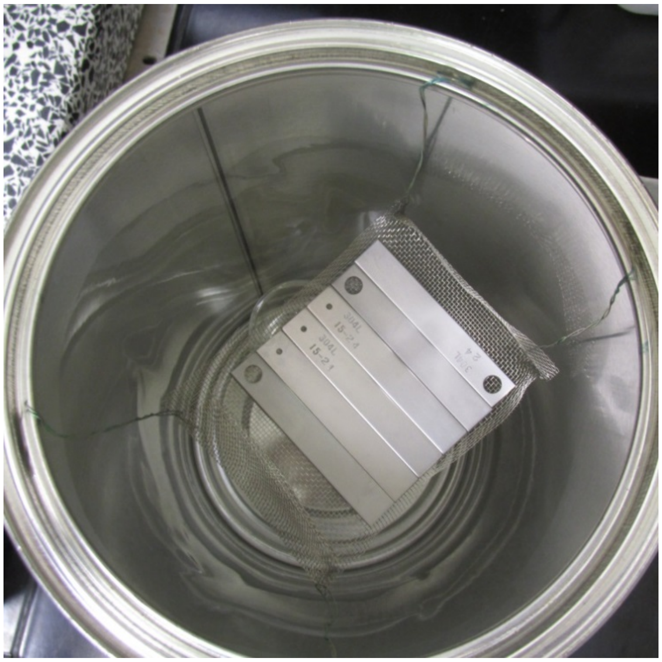

Figure 10: Vapor chamber used to suspend the stainless steel coupons. This is sealed with a tight lid and placed in an air filled oven at 50 °C.

At ~ 10 months exposure of stainless steel to MEK liquid and vapor, XPS was used to examine substrates and compare them to a control sample that was not in contact with MEK. The essence of XPS depth profiling of a stainless steel corrosion layer is captured in Figure 11, which shows the atomic concentration of oxygen and iron as a function of ion sputter time on stainless steel substrate prior to nitric acid etching. As ion sputtering proceeds the underlying iron is revealed in increasing concentration. The crossover point between the iron and oxygen curves of the different substrates can be interpreted as a measurement of corrosion layer thickness. In Figure 11 longer times to the crossover point would indicate a thickening of the oxidation layer. The crossover points for ambient-exposed and MEK-vapor-exposed substrates are approximately equal (~ 7 minutes); these substrates have comparable corrosion layer thicknesses. The cross-over point for the substrate submerged in MEK is significantly shorter (~ 2 minutes); the corrosion layer is thinner for this substrate. This indicates submersion in the MEK provides a slight deterrent to oxidation of the stainless steel substrate. XPS depth profiling results here can be compared qualitatively to previous XPS work, but due to changes in sputter parameters crossover times should not be directly compared[4,5].

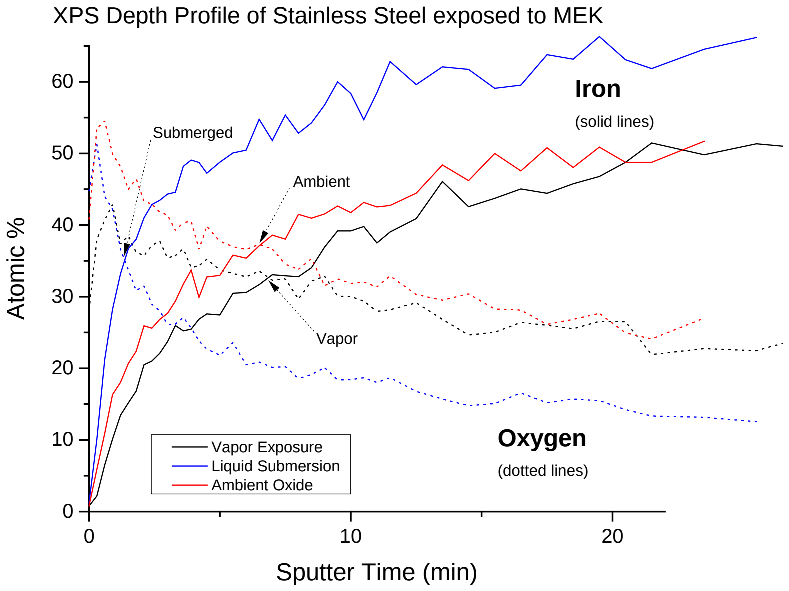

Figure 11: XPS elemental compositional comparison of oxygen and iron on stainless steel substrates, as a function of ion sputter time (depth into sample).

NEOPRENE CORROSION STUDIES

Polychloroprene is a synthetic elastomer that is commercially referred to as neoprene. Due to the presence of chlorine in neoprene some concern has been posed regarding its contact with metal substrates such as stainless steel over extended periods of time. In September of 2016 we began a contact corrosion study of neoprene and stainless steel. Initial scans with FTIR-ATR were taken of the neoprene. Originally the neoprene and stainless steel coupons were pressed into contact together using steel clamps and aluminum outer plates, at 50 °C and high humidity. After one week the container was opened and the samples were visually inspected. It was noted that the steel clamps were showing signs of degradation, and they were switched out for polycarbonate zip ties. After one month the sandwiches were inspected. Figure 12 shows the sandwiched and disassembled stainless steel substrates. Residue is observed on the coupons.

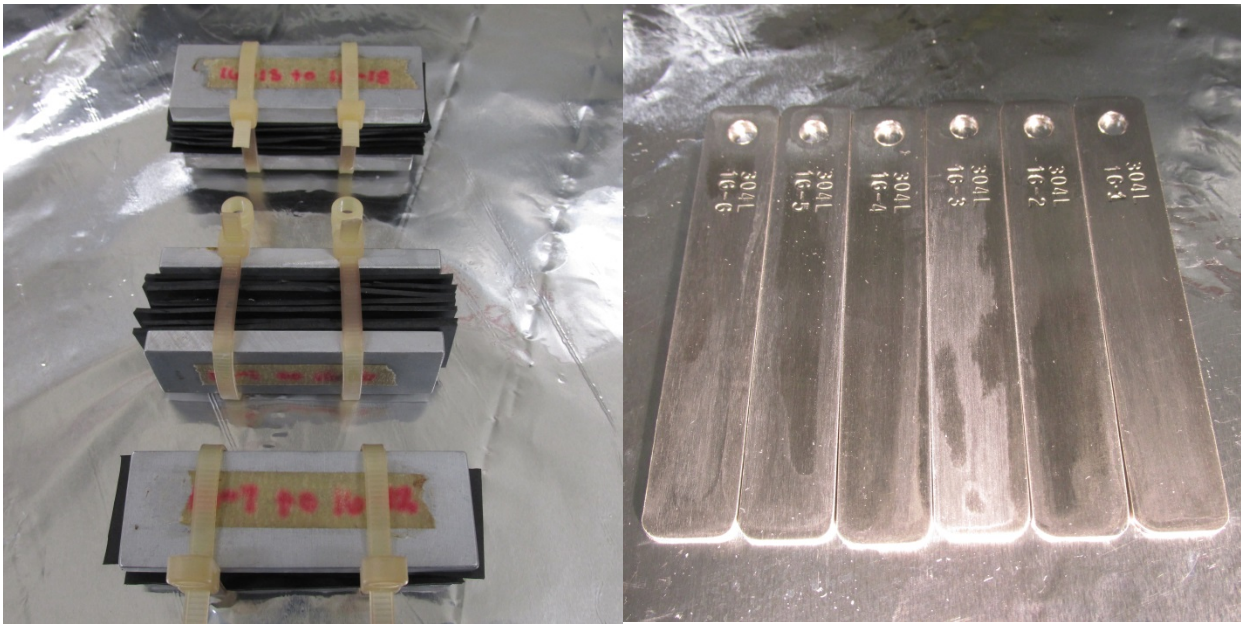

Figure 12: Left: polycarbonate zip ties used to clamp aluminum plates with stainless steel coupons alternating between neoprene strips. Right: coupons from a disassembled sandwich showing residue after one month.

During inspection after two months it was discovered that the aluminum end plates were showed signs of degradation (Figure 13, left), and they were replaced by stainless steel endplates (Figure 13, right).

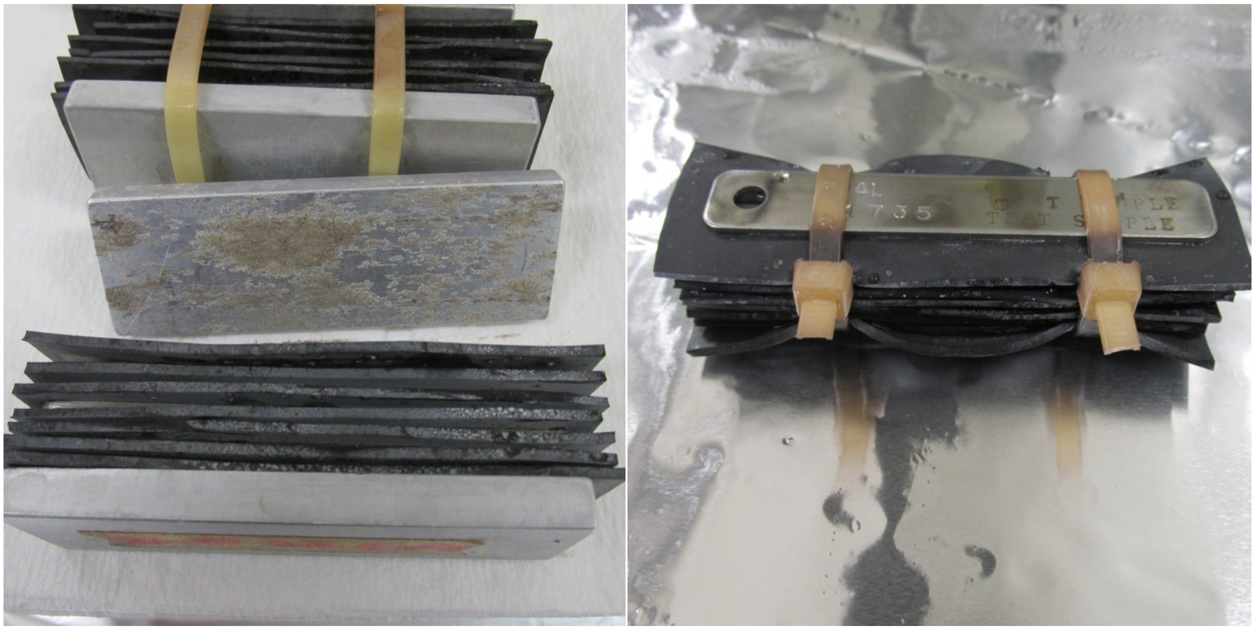

Figure 13: Left: degraded aluminum plates in contact with neoprene. Right: stainless steel end plates in sandwiches.

The degraded neoprene that had been in contact with the aluminum plates was replaced. At the three month inspection, white residue was observed to be adhered to the stainless steel coupons. The coupons looked cloudy and covered with white debris at some locations (Figure 14).

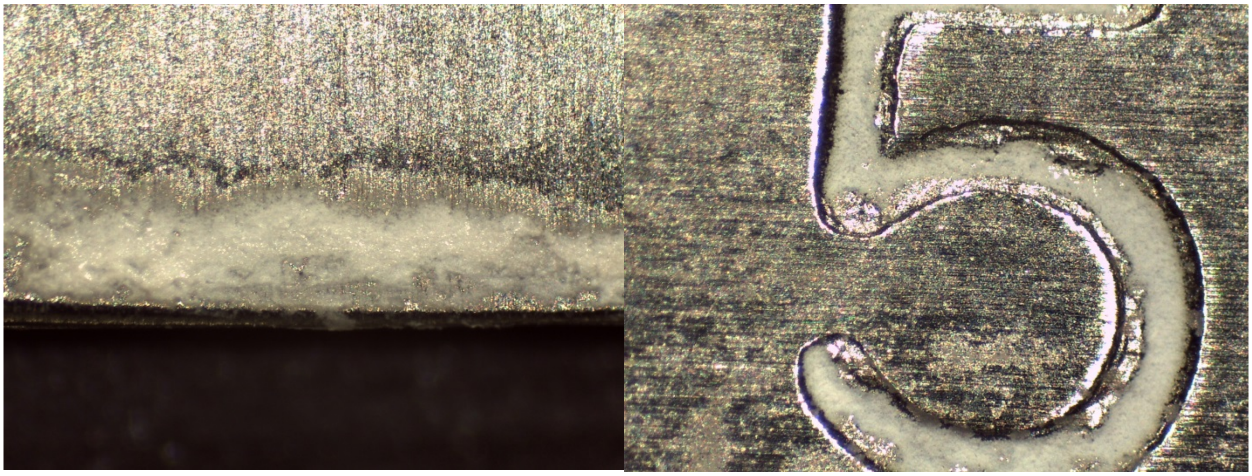

Figure 14: Left: debris at the bottom edge of a coupon. Right: white debris deposited in the crevice of the engraved ID of a coupon.

During each inspection selected coupons were weighed and then re-sandwiched for continued corrosion study. Throughout the study select coupons are acid-etched to determine precise corrosion rates. Figure 15 illustrates corrosion rates vs. time; acid cleaned coupons have a corrosion rate of effectively zero.

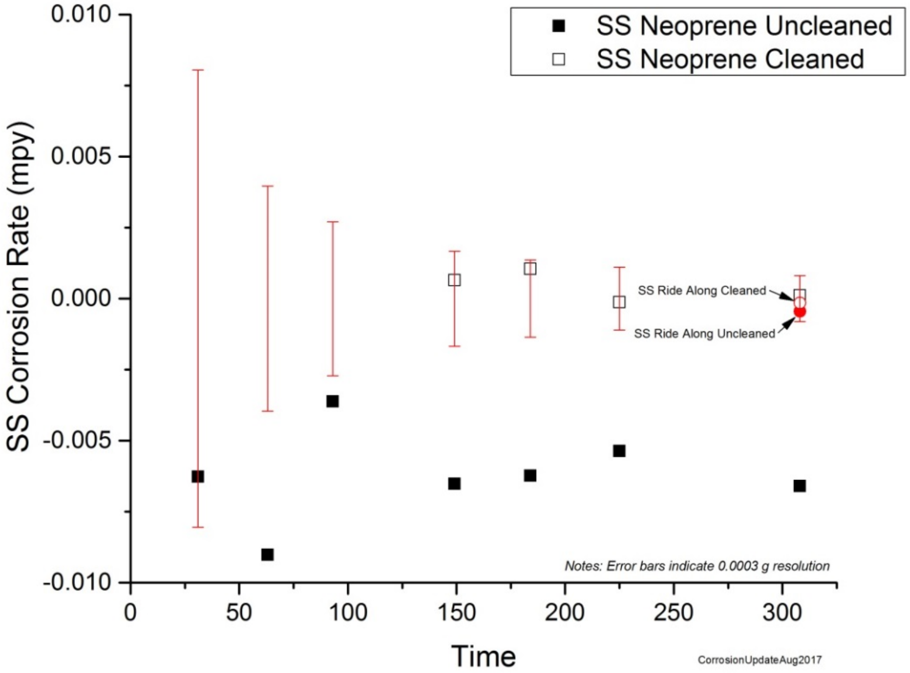

Figure 15: Corrosion rate (mpy) for stainless steel substrates pressed in contact with neoprene and exposed to humidity, at 60 ^{o}C. Error bars represent the uncertainty of the corrosion rate based on an uncertainty of 0.3 *mg* in the substrate weight. The ride-along samples were held in a glass jar in the same environment as the other samples, but not in direct contact with neoprene.

FTIR-ATR of aged neoprene were compared with fresh neoprene. A ride-along sample of neoprene (not in contact with stainless steel, but in the same container during corrosion testing) was also examined (Figure 16). FTIR of aged neoprene shows an increase in intensity at ~ 1200-1700 cm^{-1} as compared to fresh neoprene; this is true for both neoprene whether or not in contact with stainless steel. In the aged neoprene, the increase in intensity at 1500-2000 cm^{-1} could indicate polymer degradation and C=C formation.

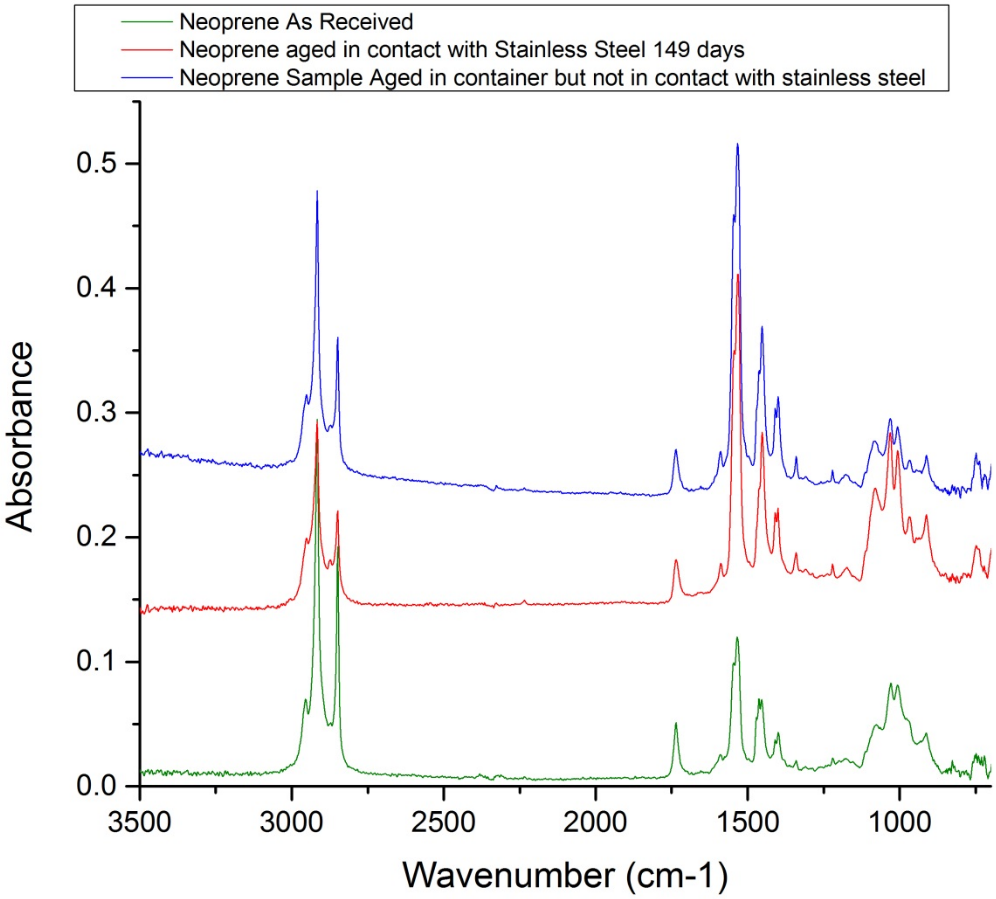

Figure 16: FTIR-ATR of neoprene. Green trace is fresh neoprene; red trace in neoprene after 149 days contact with stainless steel; blue trace is neoprene in aging container, but not in contact with stainless steel.

CONCLUSIONS

Corrosion rates of stainless steel exposed to liquid and vapor MEK at 50 ^{o}C are negligible; visually there were no signs of substrate corrosion. XPS indicates coupons exposed to MEK vapor have comparable oxide layer thicknesses as coupons not exposed to MEK. Stainless steel submerged in MEK developed a thinner oxide than for vapor exposures. Stainless steel in contact with neoprene shows a negligible corrosion rate at 50 ^{o}C and high humidity over ten months. The neoprene shows indication of compositional change by FTIR-ATR. The neoprene deposits a significant amount of residue on the surface of the stainless steel. For comparison purposes we note that corrosion rates below 0.1 mpy have historically been deemed INSIGNIFICANT from a WR *production* standpoint.

CONTINUING WORK

The corrosion study of stainless steel with methyl ethyl ketone (MEK) is concluded. The neoprene contact corrosion study with stainless steel is concluded. If neoprene is to be used at elevated temperature and high humidity, an open question is the degradation of neoprene in contact with stainless steel.

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[1] "*Stainless Steel Surface Analysis*", S. Kerber and J. Tverberg, Advanced Materials & Processes, pg. 33, 2000.

[2] "*The Effects of Electropolishing on Corrosion Resistance of 316L Stainless Steel*", S. J. Lee and J. J. Lai, J. Mat. Proc. Tech. 140, pg 206, 2003.

[3] ExxonMobil Product Safety Data Sheet, EXXONMOBIL™MEK

[4] "*Corrosion of Stainless Steel and Beryllium in NMP and HFE-IPA: FY14 End of Year Status Report*", D. Kelly, A. Longhair, and B. Cordova, LA-UR-14-27267.

[5] *"Stainless Steel and Beryllium Corrosion Studies: FY15 End-of-Year Status Report*", D. Kelly, A. Longhair, and H. Milenski, LA-UR-15-27590.