

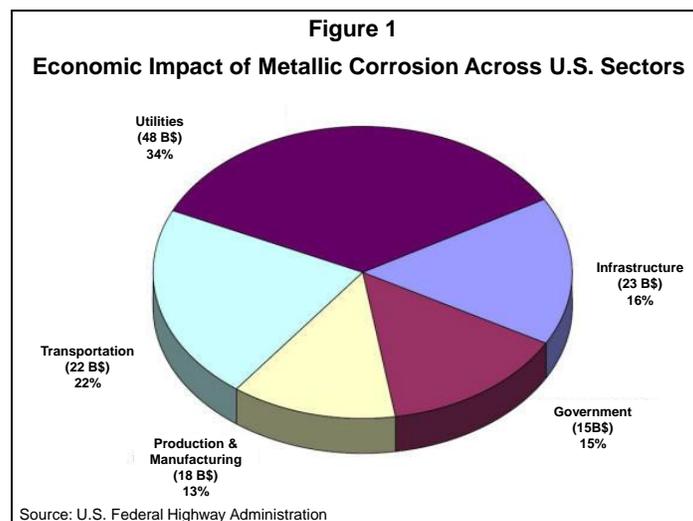
# Radiation Curable Components and Their Use in Corrosion Resistant Applications

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**Abstract:** This paper examines the use of acrylate monomers and oligomers in coatings intended to protect metal surfaces from corrosion. Using the ASTM B117 salt spray standard, a study was conducted to determine the relative effectiveness of acrylate structural classes in retarding metal corrosion. The study also investigated the impact of formulary and application factors on anti-corrosion performance.

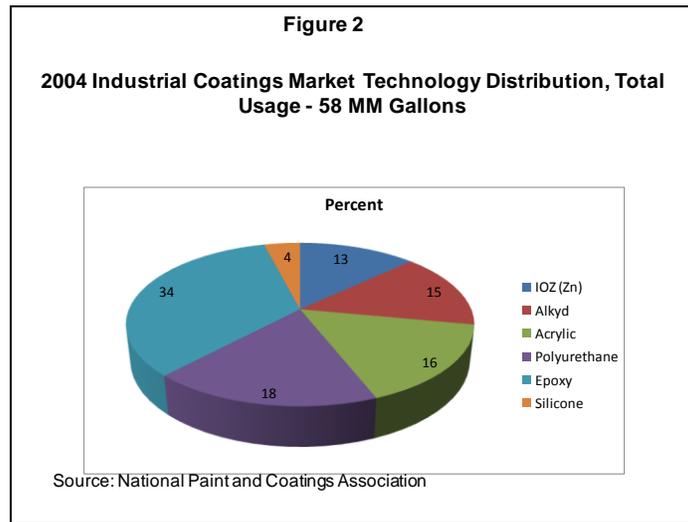
**Introduction:** Corrosion is a process by which a material may gradually wear away, usually by a chemical action. Metal corrosion is a natural oxidative process that results in an undesirable outcome, i.e., rust. Examples are common – from marine, structural, and architectural applications to residential fencing and automobiles. We are continually exposed to its impact, from superficial to severe.

The cost of poor corrosion resistance is dramatic, as determined in a 2002 study by the U.S. Federal Highway Administration. As shown in **Figure 1**, the study determined the estimated direct cost of corrosion in the U.S. to be a staggering \$276 billion or approximately 3.1% of the nation's gross domestic product. The transportation and utilities sectors received the greatest impact.

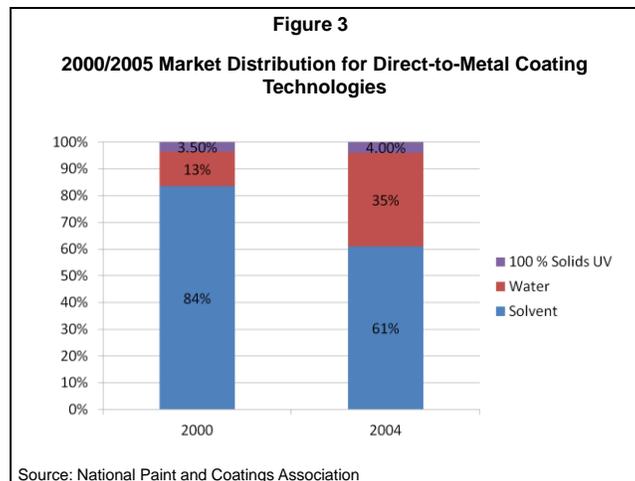


**Contemporary Coatings:** A number of chemistries and cure mechanisms are currently employed in corrosion protective coatings. These range from alkyd and epoxy ester coatings that are baked or air dried to promote crosslinking. Also used are solvent-borne two-part coatings employing polyurethanes or latexes based on vinyl, acrylic or styrenic combinations.

The industry has been trending toward more environmentally friendly water based compositions, including aqueous alkyds, epoxy esters, polyesters, and polyurethanes. High solids or powder coatings based on vinyl, polyester, or epoxy ester compositions are also favorable alternatives. **Figure 2** provides a breakdown of the chemistries used in the industrial segment in 2004.



**Figure 3** shows the trend toward “green” technologies through the use of alternatives to volatile organic compounds (VOCs). In 2000 and 2005 surveys conducted by the National Paint and Coatings Association, waterborne coatings in direct-to-metal applications rose from 13% to 35%. The same survey showed growth in 100% solids coatings based on acrylate monomers and oligomers.

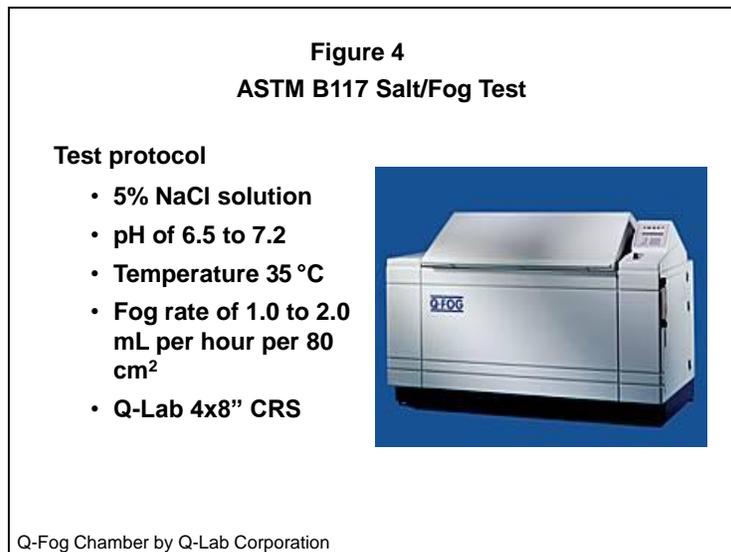


# Investigation of UV/EB-Curable Products in Corrosion Resistant Metal Coatings

**Overview:** Current uses for UV cured direct-to-metal corrosion resistant coatings include those that are applied to pipe and tubing, fencing, coil stock, and metal drums. These coatings are also used in rigid packaging applications, where they shield the inks on 2 and 3-piece beverage cans and provide environmental protection for the cans during processing, shipping, and handling. The survey cited previously suggests there may be substantial growth opportunities for corrosion resistant “green” coatings based on UV/EB curable acrylate chemistries.

## Objectives and Corrosion Resistance Test Protocol:

A long-term project was initiated to better understand the corrosion protective performance of coatings formulated from various types of acrylate monomers and oligomers. This was accomplished by coating cold rolled steel (CRS) panels and subjecting them to a controlled corrosive environment. The ASTM B117 protocol subjects coated specimens to a salt spray/fog atmosphere and is useful for this purpose. **Figure 4** shows the test chamber and summarizes test conditions.



## Specimen Preparation:

**Figure 5** summarizes specimen preparation, including coating formulation, application methodology, and cure conditions. Initially the study focused separately on the neat oligomers and monomers. Subsequently, blends of oligomers and monomers were evaluated in an effort to maximize performance. Where viscosities were prohibitively high, 50% acetone mixtures were made to facilitate handling and flashed off prior to curing.

Figure 5

Test Panel Preparation and Evaluation

- **Formulation:** Each monomer and oligomer tested contained 5.0 % photoinitiator (Daracure 1173).
- **Substrate:** Cold Rolled Steel (CRS)
- **Film Thickness:** 1.0 mil unless otherwise stated.
- **Curing:** 1600 mJ/cm<sup>2</sup> of total UV energy with two Hg arc lamps (400 w/in) as measured using the UV Power Puck radiometer.
- **ASTM B117:** Panels were exposed for 21 days, then visually inspected and given a subjective rating from 1-5 (5=best)

**Oligomer Evaluations:**

The oligomer test series comprised varied backbone structures, including epoxy acrylates, polyester acrylates, and specialty acrylics in acrylate monomers. **Figure 6** shows the ranking of these structures based on the ASTM B117 test protocol. A Bis phenol A aromatic (AR) epoxy acrylate was used as the control in this round of testing and received a rating of 2. Despite its hydrophobic nature, the polybutadiene acrylate performed very poorly (1 rating). The polyester oligomers performed likewise due poor adhesion caused by high functionality. The best performer was an acrylic oligomer (3 rating).

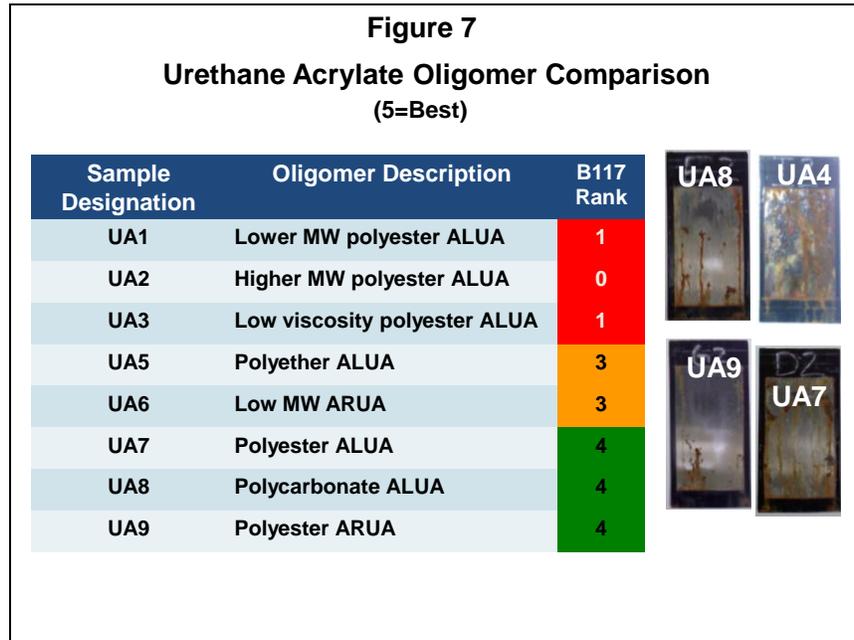
Figure 6

Oligomer Backbone Comparison  
(5=Best)

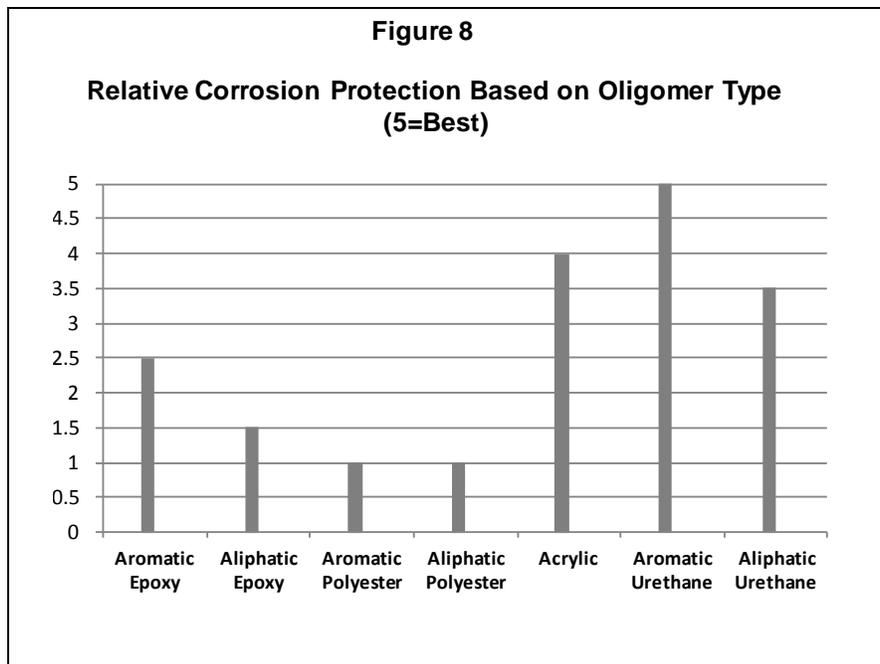
Oligomer Designation	Description	B117 Rank	Image
O1	AR Epoxy Acrylate	2	O8 O9
O2	AL Epoxy acrylate	0	
O3	Linseed epoxy acrylate	0	O6 O7
O4	Polybutadiene acrylate	1	
O5	Amine acrylate	0	O1
O6	Acrylic oligomer	3	
O7	Acrylic oligomer	1	
O8	Polyester acrylate	0	
O9	Polyester acrylate	0	
O10	Zn oligomer	0	
O11	Brominated epoxy acrylate	2	
O12	Novolac epoxy acrylate	1	

Improved corrosion resistance was observed with coatings formulated from aliphatic (ALUA) and aromatic (ARUA) urethane acrylate oligomers. **Figure 7** shows the

corrosion results for the urethane acrylate-based coatings, further distinguished by the backbone polyol, i.e., polyester, polyether, or polycarbonate. Based on this study generally, aromatic urethanes offer an advantage over aliphatic urethanes. However, the study showed that aliphatic urethanes based on polyester or polycarbonate polyols offer significantly improved corrosion resistance. Specimen UA9 in **Figure 7** is especially noteworthy.



**Figure 8** illustrates the relative corrosion protection contribution of the various oligomer chemistries.



**Monomer Evaluations:** Testing of commonly used monomers indicated that they impart less corrosion protection compared to oligomers – possibly due to significantly lower molecular weight. This performance difference may also be linked to functionality. M1 and M5 being mono functional are low in cross link density making them subject to moisture attack. In contrast M4 and M5 are higher in functionality making the film too brittle when cured resulting in poor adhesion and surface cracking. However, monomers are often a necessary component of coating formulations, and the data in **Figure 9** shows that difunctional monomers seem to offer more protection owing to a balance of cured film properties. Tricyclodecane dimethanol diacrylate (TCMDA) demonstrated the best corrosion resistance with an ASTM B117 rating of 2.

**Figure 9**  
**Comparison of Commonly used Monomers**  
(5=Best)

Sample Designation	Description	B117 Rank
M1	IBOA	0
M2	HDDA	0
M3	Tricyclodecane Dimethanol Diacrylate ( TCMDA)	2
M4	TMPTA	0
M5	PETA	1
M6	Cyclic Trimethylolpropane Formal Acrylate (CTFA)	0

Typical result  


**Impact of Corrosion Inhibiting Pigments:**The effectiveness of corrosion inhibiting pigments in coating technology is well known. However, they are not created equal. A series of pigments was evaluated individually and in combination using tricyclodecane dimethanol diacrylate monomer as a vehicle. As shown in **Figure 10**, proprietary pigment 2, at 5% by weight, achieved a perfect rank of 5 based on ASTM B117 exposure.

**Figure 10**  
**Corrosion Resistant Pigment Testing**  
(5=Best)

Inhibitor	Wt. %	B117 Rank
Pigment 1	5	4
Pigment 2	5	5
Pigment 3	3	4
Pigment 4	3	3

  
TCDMDA

  
P1

  
P2

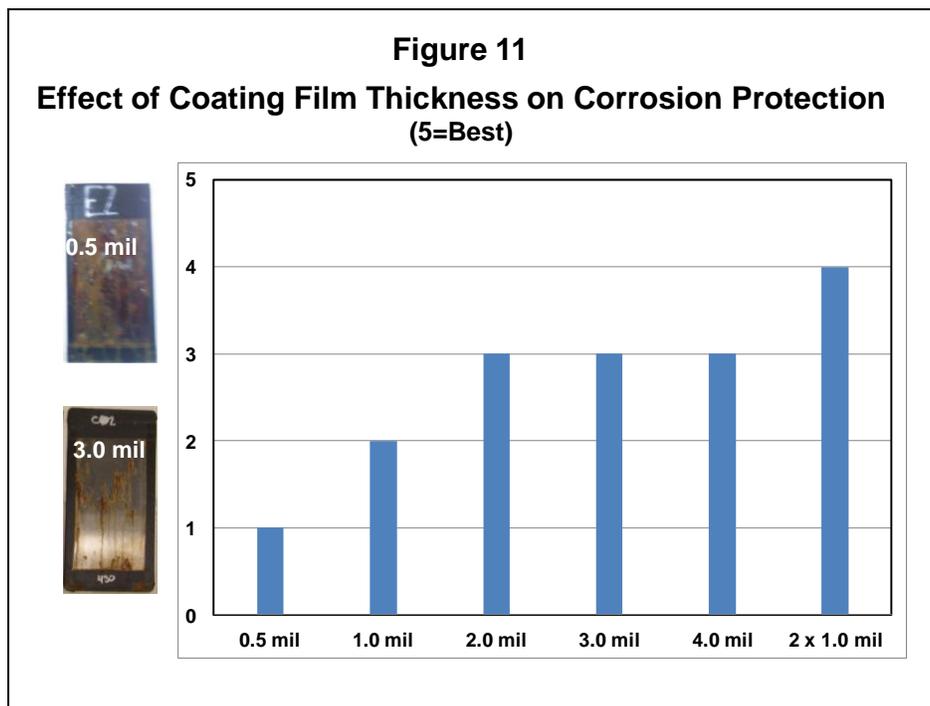
  
P3

  
P4

### Effect of Coating Film Thickness:

It is conceivable that thicker coatings might enhance corrosion protection. Again using tricyclodecane dimethanol diacrylate monomer as a coating medium, film thicknesses of 0.5, 1.0, 2.0, 3.0, and 4.0 mil were applied to test panels. Additionally, a panel was prepared in which (2) 1-mil coatings were applied, with a cure cycle following each.

**Figure 11** shows that corrosion resistance improves with coating film thickness. However, there is no added benefit from 2-4 mil. But interestingly, the specimen with (2) overlaid 1-mil films was clearly superior. It is possible that a second layer fills any voids or defects in the first, providing a higher quality coating.



**Weathering Resistance Testing:** Combating the corrosive impact of salt spray at elevated temperature was the initial focus of this project, but outdoor applications face additional degrading elements – namely UV irradiance, temperature, and moisture. QUV accelerated weathering testing intensifies the effect of these factors on coated specimens. A critical element is the spectral output of the bulb. A UVA 340 bulb was used because its output, which centers around 340 nanometers, closely replicates that of sunlight. **Figure 12** lists the conditions used in the QUV testing.

**Figure 12**

**QUV Accelerated Weathering Equipment & Conditions**



QUV unit from Q-Lab Corporation

- 8 hours of UV radiation @ 60° C.
- Followed by 4 hours dark condensation @ 40° C.
- Replace lamps every 400 hours to ensure constant UV intensity.
- UVA 340 bulb from Q-Panel. The output is from 300 - 400 nanometers centered at 340 nm.

Coatings exposed in the QUV apparatus may have a tendency to yellow over time. This yellowness index (YI) was measured initially and every 100 hours up to 1000 hours per ASTM E313-98. QUV test panel preparation and curing conditions are shown in **Figure 13**.

**Figure 13**

**QUV Test Panel Preparation & Cure Conditions**

**Urethane Acrylates:**

- Oligomers were tested “neat”
- Tested with and without hindered amine light stabilizers (HALS) & light absorbers
- With corrosion inhibiting pigments
- Photoinitiator: TPO at 3%

**Substrate:**

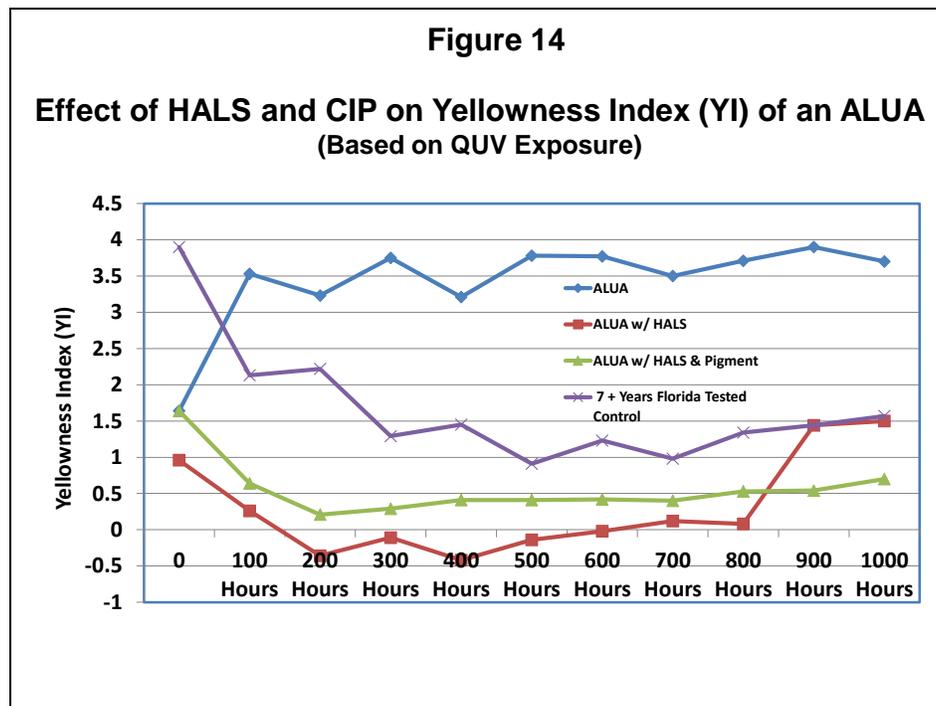
- Cold roll steel with E.coat/primer and white basecoat

**UV Cure:**

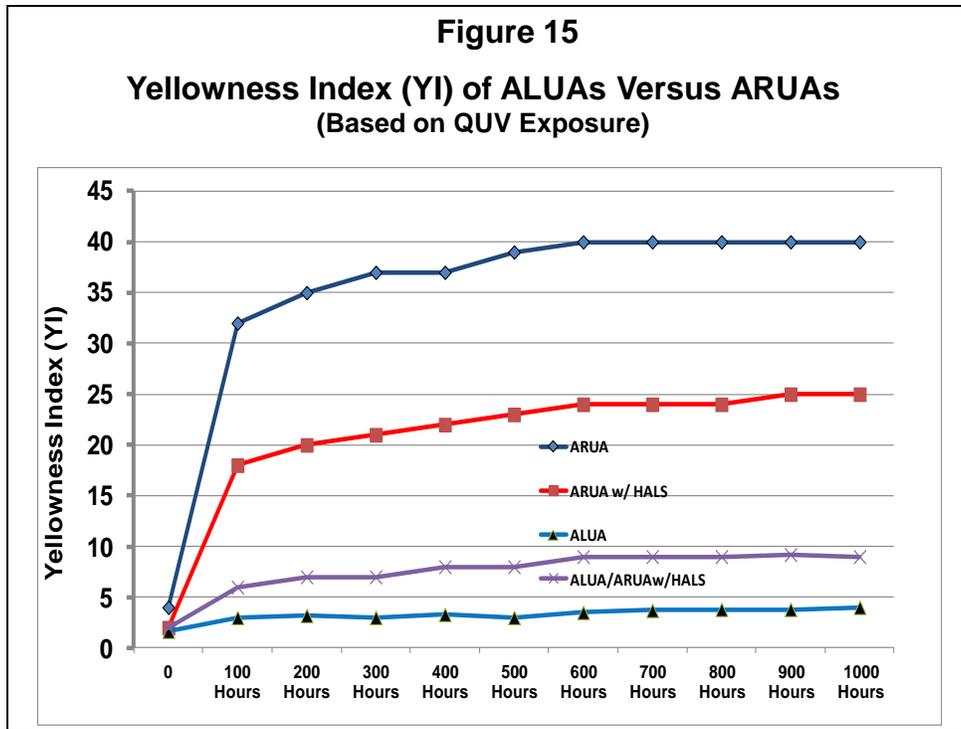
- Power Puck, Total of A,B,C and V = 4.5 J/cm<sup>2</sup>
- 600 W/inch Fusion V lamp @ 25 fpm - in air
- 600 W/inch Fusion H lamp @ 25 fpm - N<sub>2</sub>

**Film Thickness: 35-45 microns**

QUV testing was conducted on the most corrosion resistant aliphatic urethane oligomer in the previous study to establish a baseline. This oligomer was tested neat (without additives), with the addition of a HALS and with a mixture of a HALS and corrosion inhibiting pigment (CIP). As shown in **Figure 14**, the sample with the HALS achieved a YI that represented a significant improvement over the baseline oligomer. The specimen containing the HALS/CIP mixture demonstrated similar YI results to the specimen containing the HALS alone. A second “baseline” oligomer was included in this study – an aliphatic urethane oligomer that has survived 7 years of Florida exposure. The above samples containing a HALS and the HALS/CIP mixture performed comparably to the Florida-tested oligomer.



The prior corrosion resistance study suggests that with some exceptions, ARUAs may offer performance advantages over ALUAs. However, it is well known that aromatic oligomers are more prone to yellow. QUV testing was performed in which a baseline ARUA was evaluated against an ARUA containing a HALS and an ALUA containing a HALS. The results, as shown in **Figure 15**, are as expected – the ALUA with a HALS is superior to the ARUA with a HALS, which is superior to the baseline ARUA. This experiment also examined the effect of “blended” oligomer chemistries. A specimen was initially coated with an ARUA with a HALS. After curing, a coating based on an ALUA was applied and cured. The results suggest that applying an ALUA coating over an ARUA-based formulation may be a viable means of optimizing corrosion protection and weathering resistance.



## Conclusions and Observations:

**Coatings Market Trends:** The chemistries that are used for corrosion protection vary widely, including polyurethanes, acrylics, and alkyds. Epoxy-based coatings are the most common. The industry is trending toward “green” coating technologies. From 2000 to 2004, distributions of solvent-borne direct-to-metal coatings decreased from 84% to 61%. Over this period, waterborne coatings increased from 13% to 35%. UV/EB curable 100% solids coatings represent a small but growing portion of the market for direct-to-metal coatings.

**Corrosion Protection from Acrylate Chemistries:** UV/EB curable coatings based on aromatic backbone structure resist corrosion better than their aliphatic analogs. Aromatic epoxy acrylates contribute mid-range performance to corrosion protective coatings. It was observed in this study the urethane acrylate oligomers provide the best corrosion protection. Although aromatic urethanes are generally superior to aliphatics, there are exceptions based on backbone structure. Also observed was that the proper selection and use of corrosion inhibiting pigments can greatly enhance performance of acrylate-based protective coatings. Coating application technique can also influence performance of corrosion protective coatings, e.g., two thin layers are more effective than an equivalent single layer.

## Effect of Weathering on Acrylate-Based Corrosion Protective Coatings:

It is widely known that ARUAs do not resist yellowing as well as ALUAs,

addition of a HALS to coatings based on ARUAs can dramatically improve weathering resistance making them less prone to yellowing. Over coating an ARUA-based coating with one based on an ALUA may produce a weathering advantage compared to the use of the ARUA-based coating alone. The implication is a concurrent benefit to weathering resistance and corrosion resistance. The addition of corrosion inhibiting pigments did not appear to affect weathering resistance.