Acrylated Products Designed for Formability and Adhesion Enhancement in Direct-to-Metal Applications

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Abstract: Direct- to- Metal (DTM) applications require reactive materials having the correct balance of physical properties including both flexibility and toughness. These features are necessary to ensure that the finished part will withstand the rigors of forming and process handling with scuffing and surface abrasion. Also the final coating must adhere to a wide variety of metal types that may have surface contamination that make adhesion a challenge.

Introduction: This work will investigate and report the performance results of acrylated monomers and oligomers when subjected to typical end-use tests designed to measure the flexibility and adhesion characteristics of coatings. Oligomers having adhesion promoting characteristics will be tested alone or in combination with monomeric acid functional adhesion promoters to determine the best type of oligomer to use for a given substrate. Also the correct level of addition of the adhesion promoters will be determined to obtain optimum performance results. In addition moisture resistance will be explored as it relates to oligomer type.

Another significant development in the can manufacturing industry has involved the elimination of Bisphenol A (BPA) from coatings that are intended for food packaging applications. The performance benefits of polyester acrylate oligomers will be highlighted compared and contrasted to those of Bis A epoxy acrylate oligomer. Each of the formulations used in this study are in fact BPA free.

Experimental: An application area has emerged over the last several years that entail the use of radiation- curable coatings that are applied to a variety of metal surfaces. The usual standards of scratch and abrasion resistance are required. But the task is made more difficult as these coatings are required to adhere when applied to a variety of metal substrates having differing surface properties that can negatively impact adhesion. In addition, if these coatings are used for cans and rigid packaging, not only is adhesion required but a degree of flexibility is needed to withstand the rigors of the manufacturing process that result in the finished metal container. Heat and moisture resistance is also a factor when considering the retort process associated with food packaging or if coating of pipe that will be used outdoors.

Two groups of proprietary products have been developed to meet these difficult standards. The first is a series of phosphate acid ester monomers that are best used on an additives basis. They range in functionality from mono - tri with differing levels of acid content. For discussion purposes they are described as acid functional monomers or AFMs. The second group is best described as high molecular weight functional acrylic oligomers that have an adhesion promoter reacted into the backbone. The oligomers are di-functional and for best adhesion results should comprise from 30-50% of the final composition. For discussion proposes these are called Adhesion Promoting Oligomers or APO's. Figure 1 provides a listing of these components.

Adhesion Promoters Tested

Figure 1

- <u>Acrylated Acrylic Oligomers</u>
  - APO 20=CN820
  - APO 21=CN821
  - APO 22=CN822
- <u>Acid Functional Monomers</u>
  - AFM 50=CD9050
  - AFM 51=CD9051
  - AFM 53=CD9053

Application and Cure Conditions: The conditions selected represent those that are commonly used in the metal decoration industry. Ideally the film thickness should be kept to a minimum in the interest of cost but at the same time be thick enough that the performance properties are not compromised. This is attained at the nominal film thickness listed below. In addition the curing conditions cited are fairly common for these applications as a thin clear is applied negating the need for special fill bulbs. The radiometer type and results attained is also reported to avoid any variance in conditions that would affect film performance thus ensuring consistency of the end-use test results. Figure 2 describes the application cure conditions.

Figure2

• Coatings applied with a zero bar to yield a film thickness of 0.2-0.3 mils (5-7 microns).
• Cured using a 400 w/in. medium pressure mercury arc lamp at a conveyor speed of 100 fpm (350 Mj/sq.cm UVA, Power Puck radiometer trade mark).

Bisphenol A Free Formulation Selection: Bisphenol A (BPA) is a chemical building block that is used primarily to make epoxy resins. Bisphenol A epoxy di-acrylate has been the work horse oligomer of the coatings industry for many years because of its exceptional combination of toughness, adhesion, formability, and chemical resistance. Recently The National Institute of Environmental Health Sciences conducted a study and has expressed some concern regarding the long term health effects of exposure to BPA. Hence the can producers and formulators to the food packaging industry are moving towards BPA free systems. A family of oligomers that meets the BPA free criteria is Polyester Acrylates (PEA's). The following table offers a comparison of physical properties between a PEA and an epoxy and highlights the benefits of going to a BPA free alternative.

Besides being BPA free the PEAs offer these benefits:

1) Faster cure, tetra functionality as compared to di-functional.
2) Greater ease of handling as the viscosity of the PEA is dramatically lower.
3) Greater formulation latitude is also observed as more of the PEA can be used in the final formulation without adversely effecting viscosity.
4) PEAs are as tough as epoxies with better flexibility.
5) PEAs offer better yellowing resistance than BPA based oligomers.

Importance & Logic of Oligomer Selection
BPA Free

Oligomer Type	Polyester Acrylate	Epoxy Acrylate
Functionality	4	2
Viscosity @ 25C	70,000 cps	850,000 cps
Viscosity @ 60C	2,000 cps	4,625 cps
Modulus, psi	160,000	212,000
Tensile, psi	6,800	8,400
% Elongation	15.0	1.5
Tg C by DSC	31.2	20.9

Formulation Used for This Study: For the obvious benefits cited a PEA was selected as the major component for this formulation. The monomers selected for this study consisted of tripropylene glycol di-acrylate (TPGDA), dipropylene glycol di-acrylate DPGDA), and 3-mole ethoxylated trimethylolpropane triacrylate (3EO TMPTA). TPGDA was selected as a low-volatility and low-viscosity monomer that is commonly used for cost reasons in free radical polymerization. DPGDA is also an economical reactive monomer that can replace hexane diol di-acrylate (HDDA). It has good viscosity reducing properties and is more user friendly, having a Primary Irritation Index (PII) of 2 compared to 5 for HDDA. Ethoxylated TMPTA was also selected for its low skin irritancy
but it , offers the added benefits of higher cross-linking and enhanced surface cure. The photoinitiator used for these formulations is a polymeric alpha hydroxyl phenyl ketone blended with 2-hydroxy-2 methyl-1-phenyl-1 propanone. The surfactant was used to ensure proper wetting of the substrate. The viscosity of the base formulation is 300 cps @ 25C.

Base Formulation Used (unless otherwise stated)

Components	Weight Percent
Tetra-functional Polyester Acrylate	50.0
3EO TMPTA	14.9
DPGDA	14.9
TPGDA	14.9
Polymeric Alpha Hydroxy Ketone Photoinitiator	5.0
BYK371 (surfactant from BYK Chemie)	0.3

Substrates Used and End Use Tests Conducted: All metal test panels used were obtained from Q-Panel. Prior to coating, the panels were washed with solvent (MEK) to remove surface contamination. Substrates that are commonly used and thus selected for testing include aluminum (Alum.), tin- plated steel (TPS) and cold rolled steel (CRS).

The tests conducted on cured films are listed below. Cross hatch adhesion was selected as it relates the affinity of a given coating to a substrate. Reverse impact is interesting as it relates not only adhesion but flexibility of the coating and provides an indication of the forming capabilities. MEK resistance gives a quick indication of how well the coating is cured. The ASTM numbers are referenced below.

1) Cross Hatch Adhesion- ASTM D 3359- Using 610 tape.
2) Reverse Impact Resistance- ASTM D 2794
3) Solvent Resistance- ASTM D 5402

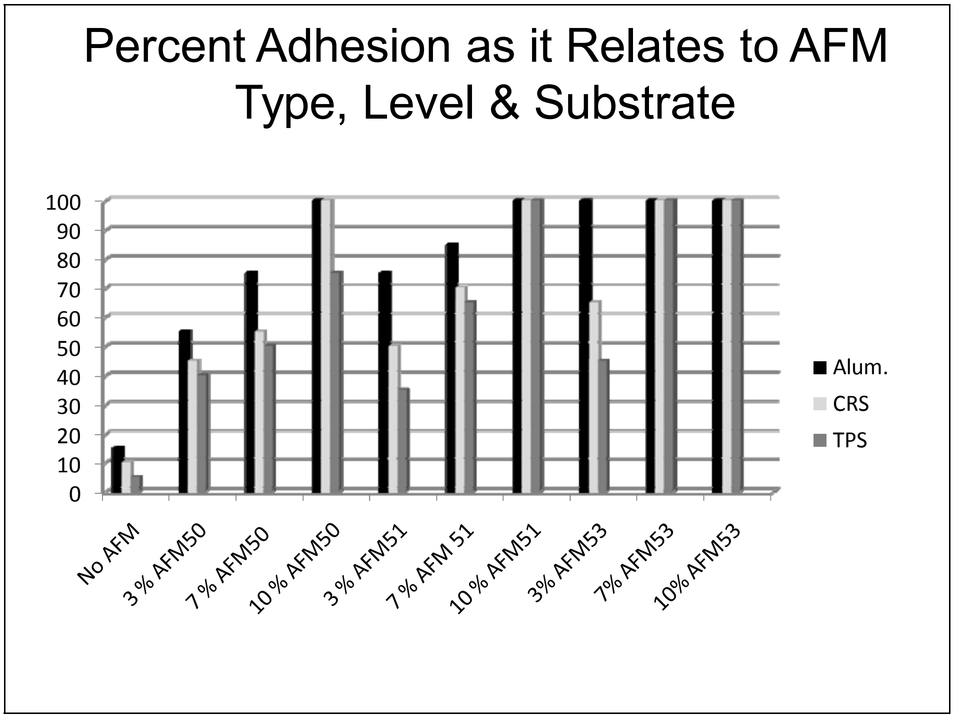
Description of Acid Functional Monomers (AFM): As a family these products can best be described as acid esters. AFM50 is a mono-functional adhesion promoting monomer that provides exceptional adhesion to metal substrates. AFM51 and AFM53 are tri-functional versions of AFM50. They offer the same adhesion promoting properties; however, owing to their tri-functionality, they provide faster cure response and greater hardness. Due to their high acid values these products are not recommended for use in formulations containing tertiary amines. Usage levels of 3% to 7% by weight are recommended. Acid values range from 120-195 mg KOH/g. The following table relates the physical properties of the monomers.

Physical Properties of Acid Functional Adhesion Promoting Monomers

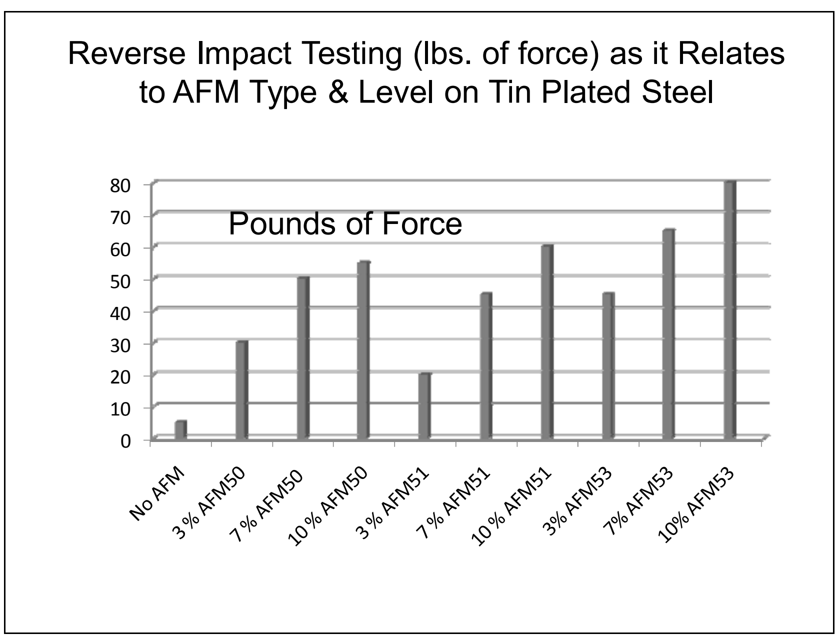
AFM Tested	Funct	Visc. @ 25C	Color	Density (g/cm3)	RI	Surface Tension dynes	Tg by DSC	Tensile Stress psi	% Elong.	1% Modulus psi
AFM50	1	20 cps	340 APHA	1.132	1.4513	33.2	-63.0 C	341	6.3	5,556
AFM51	3	250 cps	5 Gardner	1.187	1.4696	36.24	41.0 C	4,951	4.2	41,309
AFM53	3	725 cps	201 APHA	1.210	1.4711	38.7	27.0 C	1,524	10.0	41,789

Adhesion Testing of AFMs: Each monomer was added to the base formulation at 3, 7 and 10% levels. Once thoroughly mixed the coatings were applied onto each metal substrate and cured as prescribed. Upon curing the test panels were allowed to equilibrate at room temperature for one hour before conducting cross hatch tape adhesion testing. The "Control" formulation contained no adhesion promoter.

The trend is consistent with each AFM. As the concentration of AFM increases the adhesion improves. The results also indicate the aluminum is relatively easy to adhere to. Adhesion to CRS is more difficult and adhesion to TPS is the most difficult. When adhesion performance of each AFM is examined, AMF53 yields the best overall results. The optimum level addition is between 7% and 10%. The following graph details the test results.



Reverse Impact Testing of AFMs: In addition to adhesion the ability of the coating to withstand the rigors of processing is critical. Adhesion to a flat stock is relatively easy. However the metal sheets are ultimately shaped into a can body, can end or closure for a plastic or glass container. Reverse Impact Testing is a viable method to predict forming performance after cure. The following graph relates the results.



Reverse Impact (RI) was tested on TPS panel as this substrate proved to be the most difficult to adhere to. As the name implies reverse impact testing entails dropping a weight on the reverse side of the coated test panel. As the height from which the weight is dropped increases the impact force and the deformation of the test panel and coating also increases. The impacted area is then inspected for signs of cracking or adhesion loss of the coating. The highest force at which no coating damage is detected is reported. The data shows that as the concentration of AFM increases the force also increases. AMF53 yields the best overall performance exhibiting the greatest RI value on the most difficult substrate.

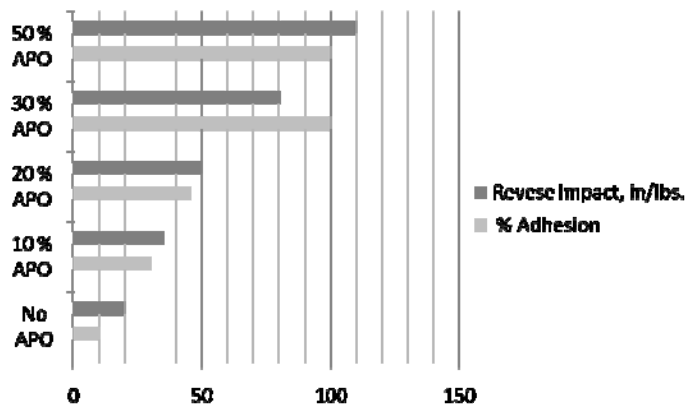
Adhesion Promoting Oligomers (APOs): APOs can be described as high Mw acrylate functional acrylics. Being of a high Mw, they are higher in viscosity ranging from 3,000 cps to 8,000 cps @60C. These APOs contain adhesion promoting materials that are reacted into the backbone of the oligomer structure; thus, they are less impacted by moisture sensitivity. APOs are not to be used as additives but should comprise from 30-50% of the final formulation. As they are not acid functional, they can be used in combination with amines unlike the AFMs. Another obvious difference between the oligomers is the color. APO20 has a Gardner color of 4 while APO 21 and 22 has APHA colors of 34 and 70 respectively. The following table lists the physical properties of the APO’s tested.

Physical Properties of Acrylated Acrylic Adhesion Promoting Oligomers

APO Tested	Functionality	Viscosity @ 25C	Viscosity @ 60C	Color	Density (g/Cm3)	Refractive Index	Tg by DSC
APO20	2	38,750 cps	3,312 cps	4 Gardner	1.03	1.4814	28.0 C
APO21	2	54,600 cps	3,718 cps	34 APHA	1.04	1.4703	56.23 C
APO22	2	424,000 cps	7,675	70 APHA	1.05	1.479	63.5 C

APO Adhesion Results: Each of the APOs was added to the base formulation at concentrations ranging from 10 to 50%. Tin- plated steel (TPS) was selected for as the test substrate as it has been shown to be the most difficult substrate to adhere to. The coatings were applied and cured under the conditions previously outlined. MEK resistance, reverse impact and cross -hatch adhesion were tested. The following graph the performance as it relates to APO concentration. The data related is typical for each APO. Adhesion and reverse impact performance improves as APO level increases. Optimum level of addition for good adhesion is 30%. Reverse impact continues to rise as more APO is added.

Typical Adhesion & Reverse Impact Results on TPS as it Relates to APO Concentration
MEK Rub Resistance > 200 regardless of APO level



Moisture Resistance Testing of APOs: Another Important requirement for DTM applications is the ability of the coating to maintain its properties when exposed to water. This exposure may occur during the processing phase of packaging or in outdoor use. The coating must maintain adhesion, while exhibiting no signs or softening or surface erosion. The table below illustrates the formulations used for this testing.

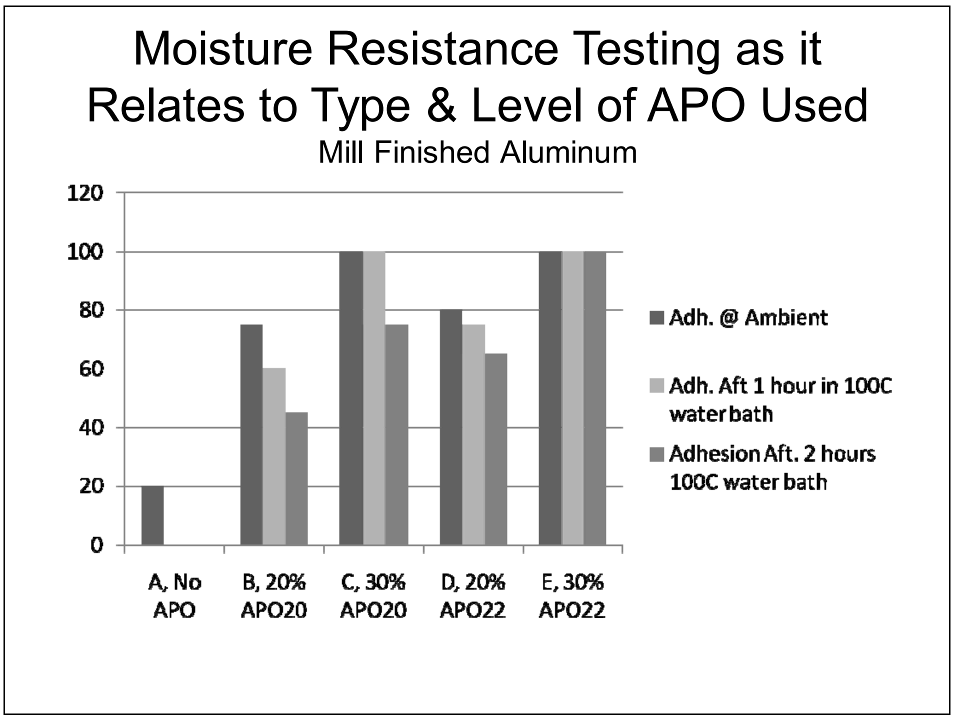
Moisture Resistance Testing on Mill Finished Aluminum
(PI Used 5.0 % Esacure KIP100F)

Formulations Tested

Formulation Variable	A	B	C	D	E
			Oligomer Wt. %		
Di-functional Aliphatic UA	40	20	20	20	20
APO Level	0	20 APO20	30 APO20	20 APO22	30 APO22
			Monomer Wt. %		
APO 53	15	5	5	5	5
DPGDA	15	25	20	25	20
PEA	25	25	20	25	20

In this case the APOs are tested in combination with a urethane acrylate oligomer. The APO used was either APO20 or APO22 at 20 and 30 percent levels of addition. The “Control” is formulation A. This contains no APO. Each coating was applied to mill finished aluminum at a film thickness of 12 microns and cured as earlier described.

Upon curing, adhesion was tested initially and after 1 hour and 2 hours submersion of the test panels in water at 100C. When APO20 was added at the 30% level, adhesion immediately after cure and after 1 hour in 100C water was excellent. After 2 hours the adhesion dropped to 75%. APO22 seemed to have better adhesion overall and excellent adhesion after 2 hours submersion in 100C water. The “Control” formulation with no APO had only 20% adhesion initially and no adhesion after water exposure. The following graph relates the results.



Another measure of how well a formulation or an individual component will resist moisture degradation is to conduct accelerated weathering testing. In this case the “neat” oligomers were placed in a QUV test chamber. The cured panels were tested right after cure and at 100 hours intervals out to 500 hours QUV exposure. The yellowness index (YI) and gloss retention were recorded. The YI measures the degradation of the coating upon exposure to sunlight while gloss retention measures the material’s resistance to micro-cracking (heat and light effects) or surface erosion related to the effects of moisture exposure. The following table details the cycling conditions for the QUV test chamber along with specifications for the measuring devices used and the test methods employed.

QUV Testing of Acrylated Acrylic Adhesion Promoting Oligomers

QUV Cycle Conditions

- UVA 340 from Q-Panel, 300 - 400 nm centered @ 340nm
- Compares favorably to natural sunlight in this region.
- 8 hours UV radiation @ 60 C.
- Followed by 4 hours dark condensation @ 40 C.
- Lamps replaced every 400 hours to ensure constant UV intensity

Gloss & Yellowness Index Measurements

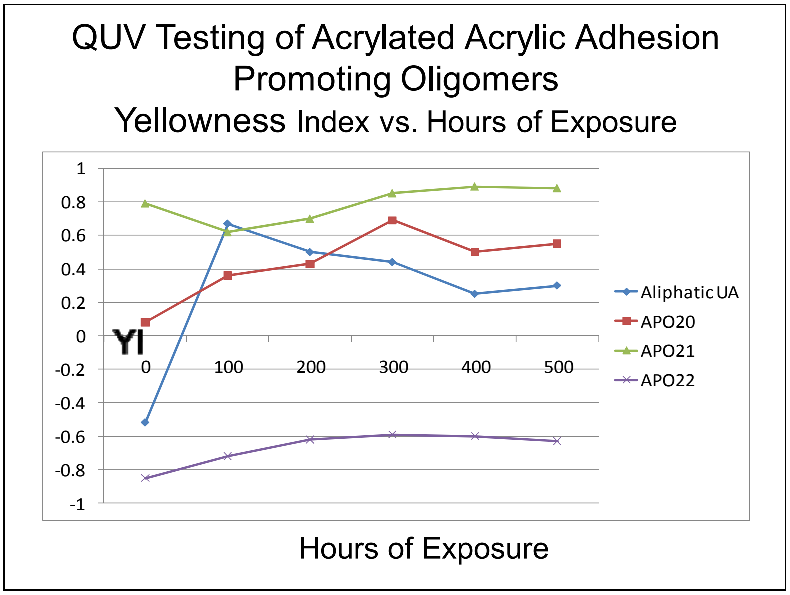
- BYK Gardner, Micro-Tri- Gloss Meter @ 60 Degree Angle, ASTM D 523
- BYK Gardner, Yellowness Index, Model 6830, ASTM E 31

QUV Test Panel Preparation: This testing differs from the previous conditions outlined as the individual components are tested alone not as additives to the base formulation. This will give a better indication of how the base oligomer performs. To enhance the ability to measure the YI the oligomer containing only a photoinitiator (PI) was applied to a white base-coated panel at a film thickness of 1.5-1.75 mils. The curing conditions were also altered to better match the wavelength absorbency characteristics of the PI. The following table details the exact conditions.

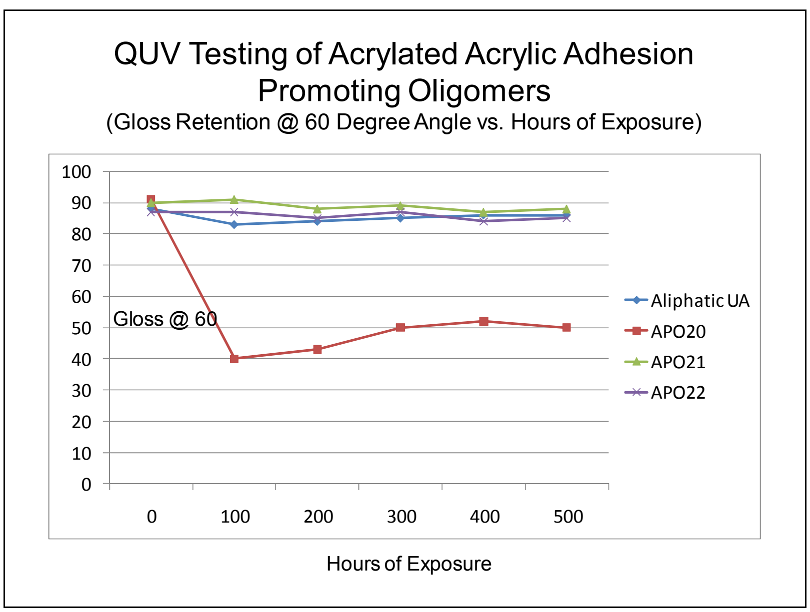
QUV Test Panel Preparation, Cure & Application Conditions

- Clear coats:
  - Neat Oligomers
  - Photoinitiator: TPO at 3%
- Substrate:
  - Cold roll ed steel with E.coat/primer and white basecoat
- UV Energy: Combined UVA, B, C and V Regions, Power Puck Radiometer, 4.5 J/cm^2 ,
  - 600 W/inch Fusion V lamp @ 25fpm – in air
  - 600 W/inch Fusion H lamp @ 25fpm - N_2
- Film thickness: 1.5-1.75 mils

QUV Test Results show that the APOs in terms of yellowing resistance perform very well when compared to the “Control” urethane acrylate (UA). This UA has in fact has passed 5 years Florida exposure, inland south facing at a 5 degree angle.



Although none of the oligomers yellowed significantly APO20 does show a dramatic loss of gloss after 100 hours QUV exposure. Visual inspection showed that this is not due to micro-cracking as noted with highly functional urethanes, but is rather a loss of gloss related to surface erosion from moisture exposure.



Conclusions/Observations:

BPA -Free: Firstly this investigation has shown that improvements can be made to the formulation by using a PEA in place of a BPA containing epoxy acrylate. Besides the obvious advantage of being a BPA -free formulation, it provides greater formulation latitude and enhanced performance benefits by having:

1) Dramatically lower viscosity thereby increasing the ease of handling and eliminating the need to heat the oligomer to transfer from one container to another.
2) Greater formulation latitude by allowing more high weight molecular oligomer to be added to the formulation to improve performance without adversely impacting blending ease or increasing application viscosity.
3) Faster UV cure as the PEA is tetra-functional verses difunctional for the epoxy acrylate.
4) PEA's have inherently better yellowing resistance when compared to epoxy acrylates.

Acid Functional Monomers, AFM: These components offer several advantages including:

1) Ability to promote adhesion to a variety of metal substrates, including aluminum, cold - rolled steel and tin- plated steel.
2) Not limited to metal adhesion as these monomers have been added to formulations that are applied on other substrates, such as wood and plastic with positive adhesion results.
3) Low level of addition required to impart good adhesion. Testing has shown that the optimum level is approximately 7 percent, resulting in minimal impact on other performance properties.
4) Testing has also demonstrated that these materials not only improve adhesion to the base substrate, but in applications, such as wood, where multiple coats are applied, greater intra-coat adhesion was noted.

It should be noted again that AFM's should not be used with amines as instability may result.

Adhesion Promoting Oligomers, APO: These oligomers work best when they are the major or one of the main components of the formulation. Testing has demonstrated that the APO should comprise between 30 to 50 percent of the formulation. They do however offer the following benefits:

1) Improved moisture resistance as demonstrated by the water submersion test, resulting in 100% cross- hatch adhesion and in QUV exposure offering comparable yellowing resistance and gloss retention to that of an aliphatic urethane acrylate that has passed 5 years exposure in Florida.
2) Improved formability as demonstrated by higher reverse impact values on TPS.
3) No amine sensitivity as with the AFM.