"UV CURABLE PRODUCTS WITH SUPERIOR OUTDOOR DURABILITY"

William R. Schaeffer, Catherine Leroy, Ming Fan
Sartomer Company, Inc.
502 Thomas Jones Way
Exton, PA 19341

ABSTRACT

Previous work has focused on the weathering performance of aliphatic urethane acrylates based on molecular weight and composition as it relates to gloss retention, yellowing and mechanical properties as a function of accelerated weathering exposure via QUV. In this study we will further this work by concentrating on new urethane acrylate oligomers tested by using a Q-Sun Xenon Test Chamber which has wider acceptance in the automotive industry and comparing and contrasting this data to accelerated out door weathering conducted in Arizona.

INTRODUCTION

Ultraviolet (UV) curing has already enjoyed a healthy growth in numerous industrial applications, such as coatings, adhesives, inks and electronics on a wide variety of substrates. Fast curing, excellent film properties, and essentially no volatile organic compounds are the major benefits. In contrast, conventional solvent borne thermal curing processes are under increasing pressure from regulatory agencies to limit the amount of solvents released into the environment.

Major advances in the raw materials area in terms of monomers, oligomers and photoinitiators (PI) make this technology suitable for coatings on plastic parts that are used on the exterior of the automobile. However, due to their excellent long-term durability characteristics, they are not limited to this application, They are also ideal for other industrial segments, ranging from aerospace to sporting equipment and solar control films.

An accelerated weathering device (Q-Sun 3100) was used in a laboratory for this study. For industrial coatings, the most reliable and widely used weathering data is gathered by exposure of up to five years in a harsh outdoor environment such as seen in Florida or Arizona. However, the long exposure time required to evaluate coating durability hampers the need to study chemical changes based on a wide range of formulation components. As a result it is common practice to develop new chemistry and make significant formulation changes based on the data from laboratory accelerated weathering tests.

This paper will focus on laboratory accelerated weathering performance of a series of commercial aliphatic urethane oligomers with vastly different backbone structures. Results of the evaluation will then be compared to the results attained in an accelerated test conducted outdoors in Arizona.

EXPERIMENTAL

Materials Tested: **A listing and description of the materials tested is shown in Figure 1.** These oligomers can be best described as low molecular weight materials having an aliphatic polyester backbone structure. QUV testing has shown that this combination is essential for good outdoor durability. CN2920 was selected, as it is a widely accepted commercial product with a proven history of having excellent weathering properties. In addition this material is best known for its hardness, toughness and superior scratch resistance. In contrast, the other oligomers are highly flexible, especially CN9001. In addition to being very elastomeric, laboratory testing has shown this material to have good thermoforming properties and excellent adhesion to many plastic substrates including polycarbonate. CN991 has moderate tensile and modulus properties. These oligomers maintain these characteristics even after long-term exposure to accelerated weathering conditions, as the upcoming data will support.

Figure 1
Urethane Acrylates

Aliphatic Oligomers Tested

- CN2920
- CN991
- CN9001
- New commercial products generated as the result of this study

Test Panel Preparation and Curing Conditions: A description of sample preparation in terms of level and type of PI used, substrate, cure conditions and film thickness is listed in Figure 2.

Figure 2
Test Panel Preparation & Curing Conditions

- **Clearcoats:**
  - –Photoinitiator: TPO at 3%
  - –Oligomers - Monomers
- **Subtrate:**
  - »Cold roll steel with E.coat/primer and white basecoat
- **UV dose:** 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: 35-45 μm

To each oligomer a 3.0 % level of an Acyl Phosphine Oxide type of PI was added. This was Lucerin TPO available from BASF. This PI was selected, as it is well known for its photo-bleaching characteristics upon exposure to UV, thus imparting little or no yellowness to the cured film. Each oligomer/PI blend was then applied to cold rolled steel having an E-coat primer and white basecoat to yield a film thickness ranging from 35-45 microns.

Since the maximum absorption of the PI is between 350-420 nanometers of the electromagnetic spectrum, initial curing was conducted using a "V" type bulb. The maximum spectral output of this lamp is above 400 nanometers thus being a good match for the absorption characteristics of the PI and therefore ensuring efficient cure of the bulk of the film. Since we are curing "neat" oligomers and oxygen inhibition can be an issue, a secondary UV exposure was conducted in an inert atmosphere to enhance the surface cure properties.

Accelerated Weathering Tests: Figure 3 relates the 2 different types of accelerated weathering studies conducted. One is a laboratory method using a Xenon test chamber while the other is actual accelerated outdoor testing.

Figure3

Weatherability Tests

- **1. Accelerated Laboratory Testing**
  - Xenon Test chamber with a daylight filter = one of the best sunlight simulation
- **2. Outdoor exposure Testing**
  - Q-TRAC Testing

Accelerated Testing: This was conducted as specified in Figure 4. The SAE J 1960 test method was selected as these new products are designed to meet the rigorous standards set forth by the automotive industry. However they are not limited to this market segment and may be used whenever superior outdoor weathering characteristics are essential to the success of the application.

Figure 4

Accelerated Laboratory Testing - Apparatus

- QSUN with Xenon Lamps : Q-Sun 3100
  - **Irradiance with a daylight filter :**
    - **0.55 W/m^2 (summer light) at 340 nm**
  - **Exposure cycle : According to ASTM D6695-01 or SAE J 1960)**
    - **40 min light at 70°C with 50% RH**
    - **20 min light and water spray**
    - **60 min light at 70°C with 50% RH**
    - **60 min dark at 38°C with 95% RH**

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Q-TRAC Accelerated Outdoor Exposure: Test conditions are listed in Figure 5**.** As an integral part of this study, we attempted to correlate the results attained by accelerated laboratory weathering with the data obtained using accelerated outdoor weathering. A test method was developed whereby the normal outdoor exposure can be accelerated using a series of reflectors to collect and focus natural sunlight. During exposure the test panels receive a water spray during the daylight hours to simulate rain and high humidity conditions that would be experienced in a 5-year Florida exposure. The duration of this test is twelve months.

Figure 5

Outdoor Exposure Testing

- **QTRAC in Arizona (Q-Panel):**
  - **Exposure cycle : According to SAE J 1961-02**
    - » **Spray Cycle #1 : water spray for 3 min duration at a frequency of 4 per hour between 7 p.m. to 5 a.m.**
  - **280 MJ/m2 UV light in Q-TRAC = one year exposure in Florida**

Figure 6

Weatherability Parameters

- **Parameters :**
  - **Yellow Index :** (ASTM E 313-98)
    geometry: 45/0
    illuminant/observer: D65/10°
  - **Gloss :** (ASTM D523-89)
    geometry : 20° and 60°

Parameters Measured: To determine the weathering resistance of these oligomers Gloss Retention and Yellowness Index were measured as a function of accelerated weathering exposure in accordance with the ASTM procedures outlined in Figure 6 above. Readings were taken every 24 hours initially during the first week then every 168 hours thereafter.

Physical Property Testing: Products intended for outdoor use must not only resist yellowing and have a high level of gloss retention, as this property is a good indicator of moisture resistance, they must also have the ability to maintain their physical properties for the duration of their use. Therefore they must not become brittle or have signs of film degradation such as micro-cracking. Since the space is limited in the Q-Sun 3100, we developed an exposure method using the QUV that would replicate as closely as possible the conditions seen in Xenon Testing. We prepared test panels that were monitored for film strength and flexibility measuring modulus, tensile and elongation at break expressed in percent. Figure 7 relates the conditions of tests employed in the QUV to simulate those used in the Q-Sun 3100 and compares them to the actual conditions.

Figure 7

Weathering Study

QUV Conditions, 340 nm Bulb

- Method mimicing the SAE J1960 -

QSUN Cycle	QUV Cycle
Step 1: 40 min light - RH=50% - T=70°C	Step 1: 40 min light - T=60°C
Step 2: 20 min light - water spray	Step 2: 1 min light - water spray
	Step 3: 18 min light - T=60°C
	Step 4: 1 min light - water spray
Step 3: 60 min light - RH=50% - T=70°C	step 5: 60 min light - T=60°C
step 4: 60 min dark - RH=95% - T=38°C	step 6 : 1 min dark - water spray
	step 7 : 59 min dark - T=38°C

T = Black Panel Temperature

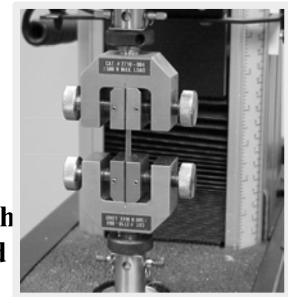
Tensile testing is conducted in accordance with the standard test method for tensile properties of thin plastic films: ASTM D882. The conditions of the test methods are described in Figure 8. Modulus is an indicator of material stiffness and is measured in force applied in pounds per square inch.

Energy is the area under the Stress/Strain and is a measure of the energy required to break the film specimen. The greater the area under the curve, the tougher the film.

Figure 8

Standard Test Method for Tensile Properties of Thin Plastic Sheeting, ASTM D 882

- **Method Applies to the Testing of Thin Plastic Sheeting & Films, <0.04 inches in Thickness**
- **Tensile Specimens Cut Into 1/2" Wide Strips With a New Single Edged Razor Blade & Metal Rule, Length >2"**
- **Typically, 22.5 pound Load Cell Used With a Gauge Length at 1" & Cross-head Speed of 1 inch/minute**
- **Rubber or Serrated Faced Pneumatic Grips to Eliminate Differences in Gripping Force**

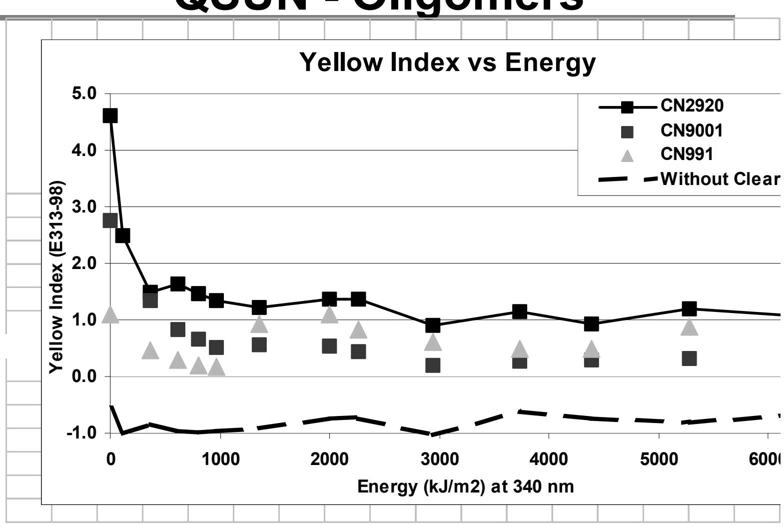


DISCUSSION AND RESULTS

Accelerated Weathering Study Q-Sun Verses Q-TRAC Testing: In this section we will compare and contrast the performance of the aforementioned oligomers in accelerated laboratory testing to the results attained using the Q-TRAC method. This represents accelerated outdoor weathering conditions in Arizona. One year in Q-TRAC is equivalent to 5 years Florida exposure. Figure 9 relates the Yellowness Index (YI) of those panels placed in the Q-Sun. The lower the YI the better the weathering resistance.

Figure 9

QSUN - Oligomers



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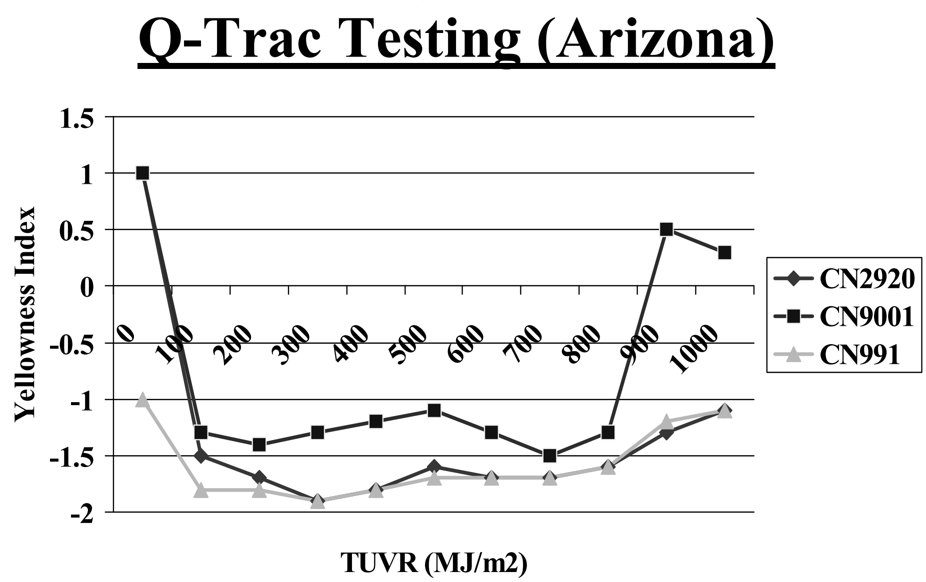
These test panels were exposed to 7,000 KJ/ Sq. M of UV energy @ 340 nanometers for a total exposure time of nearly 5,500 hours in WOM. The product designated as CN2920 is a widely accepted commercial material well known for its good weathering characteristics. The other two products were commercialized as a direct result of this testing and shows a lower initial YI as well as better overall performance for the duration of the test.

The graph (Figure 10) relates the YI of the same identical oligomers but in this case they were tested using the Q-TRAC method. The same trend continues, however, the initial YI is significantly lower for these test specimens. In addition the delta YI values are all less than –1.0 approaching -2.0 after 1,000 Mega J/ Sq. M exposures. This is equivalent to 3.6 years in Florida.

Figure 10



Based on these results one would predict with a relative degree of certainly that these oligomers are most suitable for outdoor weathering applications.

Gloss Retention: The ability of the coating to resist color change is only part of the necessary performance parameters. It is also essential that the coatings do not chalk or exhibit a significant loss of gloss for the duration of use. Along with YI testing, we also monitored the gloss of the coating at both a 20 and 60-degree angle of reflectance. These measurements were taken after the test panels were placed in the Q-Sun as well as the Q-TRAC apparatus.

The first series of graphs (Figures 11 and 12) relates the gloss values attained in the Q-Sun Test Chamber. It is interesting to note that the gloss values attained for the oligomer designated as CN991 shows what could be interpreted as a significant drop in gloss at 20 and 60 degrees. And if one were only relying on accelerated laboratory testing this product in all events would be eliminated from further testing. However this product did perform quite well in the Q-TRAC. This would suggest that laboratory testing is a good screening method but may result in over engineering of the product as it relates to actual outdoor performance.

Figure 11

Q-Sun Testing, 20 Degree Gloss

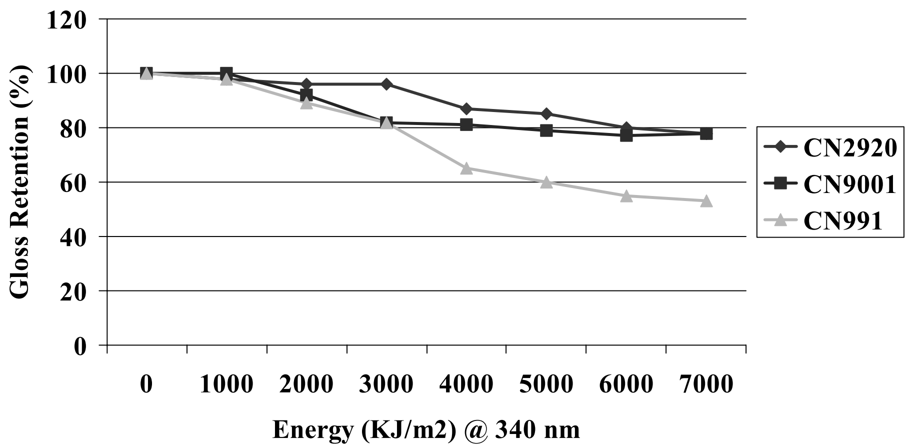
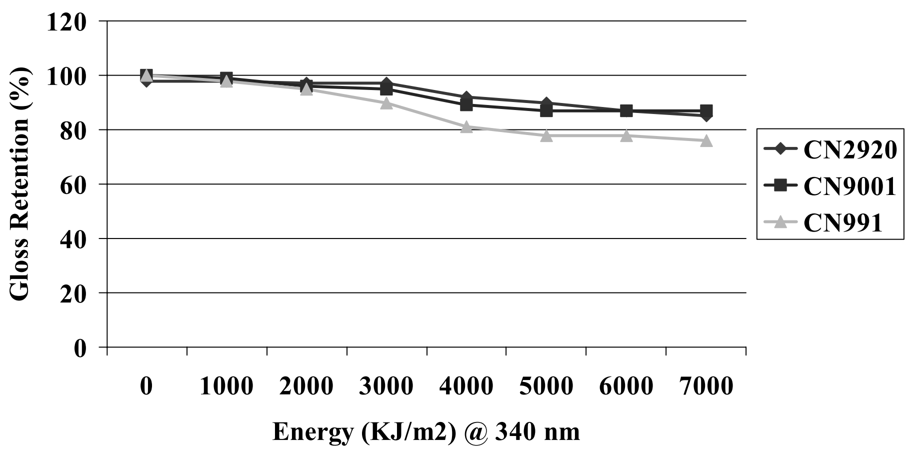


Figure 12

Q-Sun Testing, 60 Degree Gloss



As the data indicates, the 20-degree meter is more sensitive to gloss changes than the 60-degree device, and typically has wider acceptance for extremely high gloss coatings such as these.

Figure 13

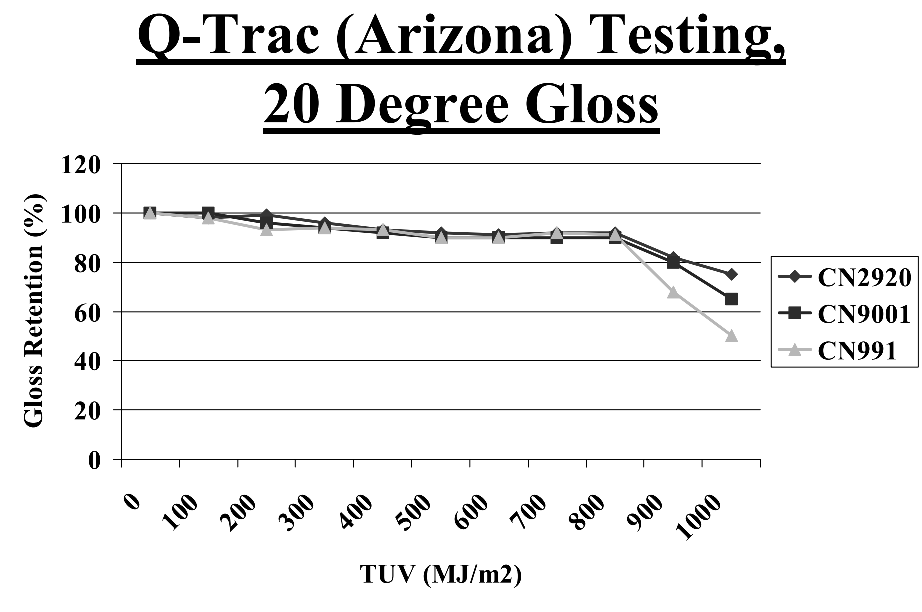
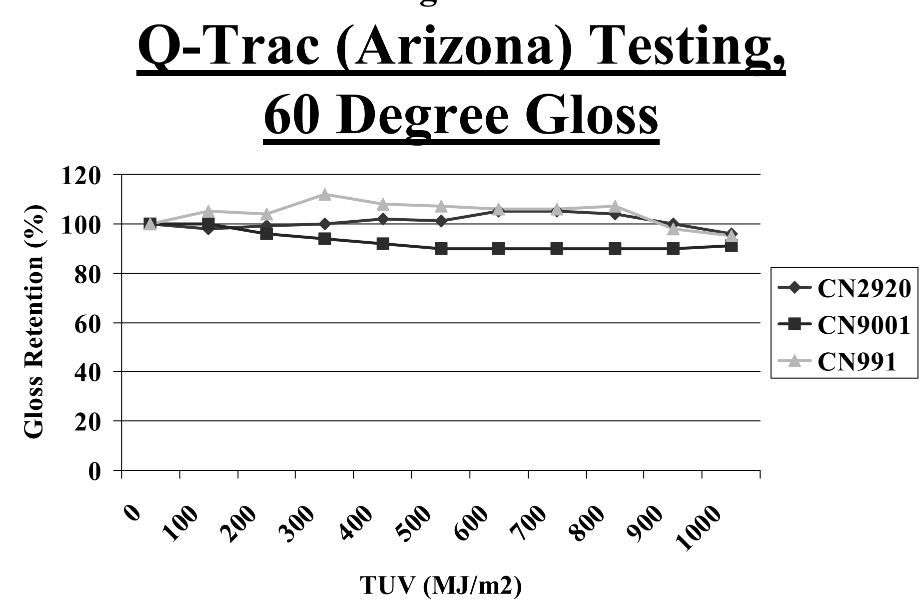


Figure 14

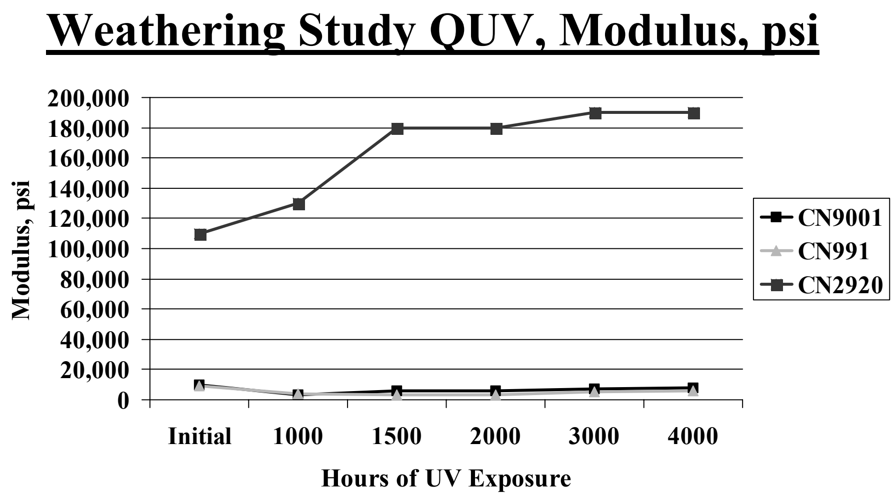


Gloss retention (Q-TRAC): Figures 13 and 14 relate the gloss data on the same series of oligomers that were tested using the Q-TRAC apparatus.

It is rather surprising to note that the same oligomers with sample panels prepared in the fashion identical to that employed in the Q-Sun test chamber have significantly better gloss retention values. This may suggest that actual outdoor weathering may not be as severe as accelerated laboratory testing. This is a useful trend, as one would also predict that if the performance were acceptable in lab testing, in all probability it would be applicable and suitable for outdoor environs.

Physical Property Testing (QUV): Not only is it critical that coatings maintain a high level of gloss without significant color change, it is imperative that the physical properties do not degrade upon long-term outdoor exposure. Panels were prepared and placed in a QUV test chamber. Instron measurements were taken initially and periodically for the duration of the 4,000-hour test. Modulus or the hardness of the coating, tensile which is an indication of film toughness and finally percent elongation @ break which is a good measure of flexibility were measured. Although the QUV is the harshest of the tests, there is ample space for samples. Therefore, if the samples hold up well in QUV, outdoor weathering performance should not be an issue. Figure 15 outlines the Modulus results.

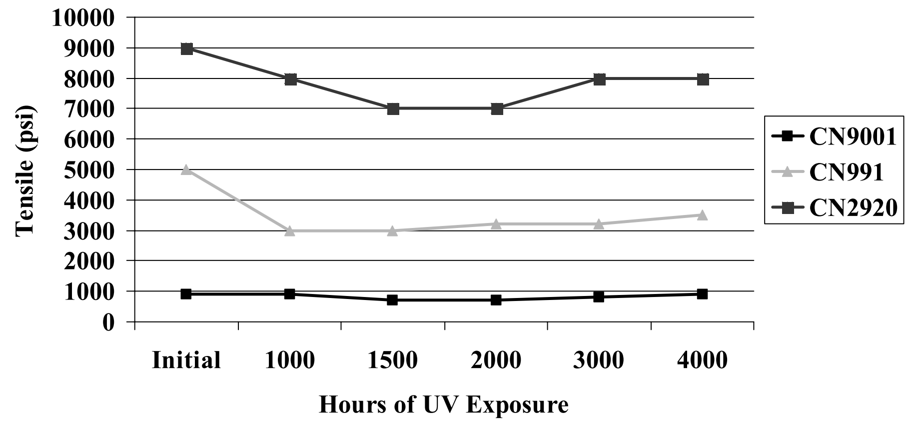
Figure 15



As the results indicate, CN2920 is by far hardest and most abrasion resistant of those tested. The modulus started very high at 110,000 psi and trended upward for the duration of the test, peaking at 190,000 psi. In all fairness to the other oligomers, values attained for CN2920 are high skewing the graph and thus masking what I would define as good performance for the other products. Their properties are also stable and remain constant for the duration of the test averaging between 8,000 and 10,000 psi. They may not be as tough but they do have other benefits that will be brought into focus as the discussion of the physical properties continues.

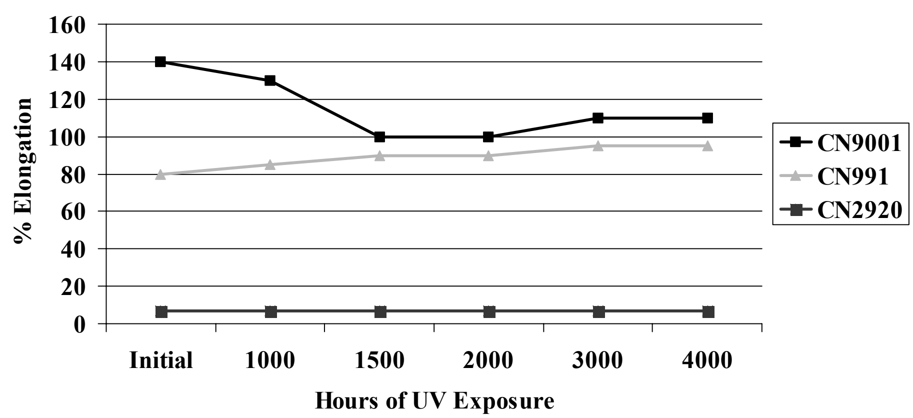
Tensile Properties QUV: Again all oligomers tested maintain a very stable profile for the duration of the test. The test also illustrates that the CN2920 type is not only the hardest but also the toughest product.
Figure 16 offers a graphic representation of the tensile properties.

Figure16
Weathering Study QUV, Tensile, psi



% Elongation, QUV: Figure 17 relates the flexibility data on these products.

Figure17
Weathering Study QUV, % Elongation

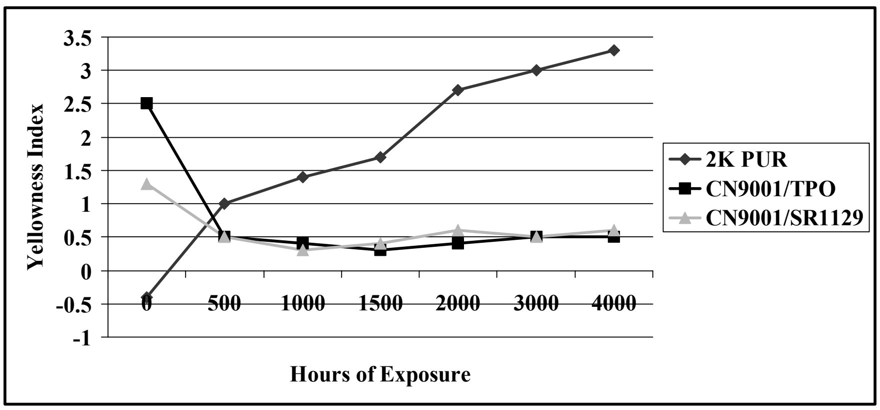


Although CN991 and CN9001 had only moderate toughness and hardness, they are both extremely flexible, having an elongation @ failure of 95 % and 110%, respectively, after 4,000 hours of QUV testing.

Photoinitiator Influence on Yellowness Index: Another important factor to developing a UV cured coating with good weathering resistance is the type of photoinitiator used. In Figure 17A a comparison of yellowing resistance is shown with 2 very different PI's in the same base oligomer. The performance is also compared to a 2-component polyurethane. The weathering was conducted in the QUV. The initial yellowness of the 2K system is quite low. However after only 500 hours of exposure, YI is twice that of the UV cured materials - nearly 7 times higher after 4000 hours. In contrast the UV cured oligomer maintains a very low level of color for the duration of the test without the addition of light absorbers or hindered amine light stabilizers that can oft times retard the rate of curing. Also the data shows that the initial YI can be reduced with the correct choice of PI.

Figure 17A

Photoinitiator Effects on Yellowness vs. 2K PUR



Conclusion: Based on laboratory testing and accelerated outdoor exposure, these oligomers have been shown to pass the rigorous standards set forth by the automotive industry. The data demonstrates and supports the suitability of these products to withstand very harsh end use conditions, without significant color change or degradation of the physical properties over an extended period of time. Both CN991 and CN9001 exhibit very high degrees of flexibility and moderate toughness. In contrast, CN2920 is a very hard, durable and scratch resistant material. The data suggests that these oligomers may be blended with one another to optimize the properties for a given application to attain a balance of hardness and resiliency. The data also supports the fact that radiation cured materials are aptly suited for exterior applications, debunking the belief that UV curable coatings by nature will not withstand exposure to the UV energy naturally produced by the sun.

In addition, we have been able to correlate the severity of laboratory testing with accelerated outdoor exposure. The data strongly suggests that QUV weathering is harsher than Xenon testing. And Q-TRAC is less severe than laboratory test methods, making them very useful screening tools, but may result in over-engineering of the coating or raw material if it is not correlated with actual outdoor results. Since these materials were tested to the very stringent guidelines established by the automotive industry these products may be used in any application where superior weathering resistance is required.

Product Features and Benefits: The tables below describe the features of the products along with typical physical properties associated with the products in the liquid state.

Figure 18 Product Features		
Product	**Class**	Features
CN991	Urethane Acrylate	Moderate flexibility, Highly resilient, High film strength, Low viscosity
CN9001	Urethane Acrylate	Highly flexible, Excellent adhesion to many plastics, Withstands the rigors of thermoforming without degradation
CN963B80	Urethane Acrylate	Extremely tough and durable, Moderate flexibility

Figure 19 Typical Physical Properties				
Product	**Appearance**	**Functionality**	**Color, APHA (G=Gardner scale)**	**Viscosity, cps @ 60 °C**
CN991	Clear liquid	2	55	660
CN9001	Clear liquid	2	1G	46,500
CN963B80	Clear Liquid	2	50	25,000

Future Work Plans: Significant progress has been made in developing and understanding how to make good weather resistant materials. We still have much to learn about how these products will behave in actual Florida weathering conditions. Our goal is to pass 5 years of testing. We will be submitting samples for testing and we will continue to develop a correlation between Q-TRAC and Florida testing.

Another part of the formulation picture is to develop new monomers and optimize existing ones that have superior weathering resistance so that viscosity of the formulation can be modified to suit the application requirements. Another hurdle is to couple all of these needs into materials the can be easily cured by low intensity light sources without sacrificing the physical and weathering resistant properties essential for the auto-refinish market.