The Use of UV Stabilizers in Aliphatic Polyurea Coatings

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ABSTRACT

End-users are willing to pay a premium for aliphatic polyurea coatings because of the need for clear, colorless materials in some applications and for color stability and color reproducibility in other applications. The added cost brings with it the reasonable expectation of premium performance; however, color stability does not guarantee mechanical (strength) property stability.

In recent tests, we found that a series of aliphatic polyurea formulations that produced non-yellowing coatings had surprisingly developed cracks after less than 200 hours of exposure in a xenon lamp-based weatherometer. This result prompted us to begin an evaluation of various stabilizers for the purpose of increasing the crack resistance of these systems. Of the nine stabilizers evaluated, one had virtually no effect on crack resistance, one increased crack resistance by 10-fold (from 100 hours to 1000 hours), four showed a 20-fold improvement (up to 2000 hours), and three of the stabilizers increased crack resistance 30-fold up to 3000 hours. These aliphatic coatings have also been compared to an analogous series of aromatic polyurea coatings.

INTRODUCTION

Previous work has shown that the use of Clearlink™ 1000, which is a relatively slow-reacting aliphatic diamine curing agent, can lead to light-stable coatings with superior physical properties. In 2000, a joint paper by Huntsman and UOP presented a detailed study on the performance of Clearlink 1000 in light-stable, isophorone diisocyanate (IPDI)-based sprayed polyurea coatings [1]. These two-component polyurea systems were applied using commercial, high-pressure, higher-temperature, impingement-mixing equipment.

Later that same year, House and Ilijevski presented a paper that examined the physical properties of several IPDI-based polyurea coatings as a function of Clearlink 1000 level, isocyanate index, and the Clearlink 1000/IPDA ratio. The effects of Clearlink 1000 on polymer morphology were also studied using Fourier-transform infrared spectroscopy and a scanning vibrating needle curemeter [2]. It was in this later paper that a new laboratory screening method, based on low-pressure static mixing, was introduced that allowed one to mimic the results of high-pressure, impingement-mixing techniques.

It is well known that aliphatic polyurea coatings are much more light stable than their aromatic polyurea counterparts. It is also generally accepted that the aliphatic coatings better retain their mechanical (strength) properties. In a recent study of some selected aliphatic coatings based on IDPI, we observed the expected superiority in gloss and color retention of the aliphatic over the analogous aromatic coatings. We were somewhat surprised, however, to find that the aromatic coatings demonstrated better retention of mechanical properties upon accelerated aging in a xenon lamp weatherometer. This phenomenon is not unknown; for example, V. Rek et al. reported the same observation in 1992 [3]. In their study, they were examining the photostability of aromatic polyurethane elastomers based on MDI to similar aliphatic polyurethane elastomers based on H_{12}MDI. Their conclusion was that photooxidation was more prevalent in polyurethane elastomers based on the cycloaliphatic isocyanate than those based on the aromatic polyisocyanate, even though the elastomers based on the cycloaliphatic isocyanate did not change color with UV irradiation. The photodegradation of the elastomers based on the cycloaliphatic isocyanate was enhanced with increasing hard segment concentration, and the samples became brittle after 100 hours of UV irradiation. The hard segment concentration was increased by increasing the ratio of isocyanate in the formulation.

Not surprisingly, we have found that the retention of the mechanical properties (especially crack resistance) of the aliphatic polyurea coatings can be dramatically extended when certain stabilizer packages are added to the formulation. In fact, Andrews et al. [4] pointed out that certain aliphatic polyurethane coatings are often stabilized with UV absorbers and antioxidants. In the present study, systems using Clearlink 1000 coupled with stabilizers from Ciba Specialty Chemicals Corp. have been used to illustrate the dramatic improvements possible in crack resistance. A weatherometer using a xenon lamp was used to evaluate the coatings.

EXPERIMENTAL

Chemicals

The materials used in this study were kindly provided by the companies listed in Table 1.

Procedure

PREPARATION OF FORMULATIONS

Preparations of the polyisocyanate side (A-side) and the resin side (B-side) were carried out at 23°C +/- 1°C. An 800-gram master batch of the quasi prepolymer was prepared ahead of time by slowly adding JEFFAMINE D-2000 to the IPDI monomer at room temperature under a nitrogen blanket. The reaction mixture was vigorously

Table 1. Materials and Suppliers List.

Materials	Description	Supplier
Desmodur® I	Isophorone diisocyanate	Bayer Corporation
Rubinate® 9495	MDI-prepolymer	Huntsman ICI
JEFFAMINE® D-2000	Polyoxyalkylene diamine, mol. wt. about 2,000	Huntsman Chemical Co.
Ethacure® 100	Diethyltoluene diamine (DETDA)	Albemarle Corporation
Clearlink™ 1000	Secondary aliphatic diamine	UOP LLC
Unilink™ 4200	Secondary aromatic diamine	UOP LLC
Stabilizers A to I	Proprietary	Ciba Specialty Chemicals Corp.

stirred during the addition then degassed under vacuum at room temperature. The quasi prepolymer was stored under a nitrogen blanket until used.

The B-side of each formulation was prepared by thoroughly mixing the isocyanate-reactive components (and any stabilizer) together in a waxed-paper cup, using a high-torque stirrer, then degassing for about 30 minutes at room temperature. The B-side was poured into one of the cartridges of a dual-cartridge static mix gun. The static mixing technique has been previously described in detail [2]. Enough of the degassed quasi-prepolymer (A-side) was added to the second cartridge to equal the volume of the B-side in the first cartridge.

The pneumatic gun was run at 80 psig (static). The extruded formulation was applied directly onto glass plates that had been previously covered with a foil-backed, fluoropolymer-based film. To insure a perfect cast, the first 10 mL of the extruded formulation were discarded (not cast), since the first liquid out of the static mixer often contains bubbles and also may not match the desired volume ratio of 1.00. Likewise, the last 10 mL were discarded. A 10-inch-wide knife-blade applicator set at 0.063 inch was used to quickly spread the formulations. The thickness of the finished coatings was about 30 mil. The polymers were demolded after reaching the tack-free point, then allowed to post cure for two weeks at 23^{o}C +/- 1^{o}C and 50% +/- 5% relative humidity before testing.

CHARACTERIZATION

The polymers were characterized using ASTM methods. Hardness was measured using ASTM Method D 2240, tear resistance using D 624, tear propagation resistance using D 1938, and resilience (Bashore rebound) using D 2632. Moduli, tensile strength, and elongation were measured using D 412.

Pot life was defined as the time when a string of the curing polymer could be pulled up about one inch from the coating using a glass rod, and the string did not break for at least 10 seconds. The tack-free time was defined as the time when the polymer was completely free of tack and the coating was thoroughly set.

The color determinations were made using an ACS PEF-CO4 dual-channel spectrophotometer. The weatherometer test procedure was based on ASTM Method G 26 and used an Atlas Ci65A xenon lamp weatherometer equipped with borosilicate filters (in and out). The dry bulb was at 45^{o}C, the wet bulb at 35^{o}C, and the wet bulb depression was 10^{o}C. The conditioning water was at 40^{o}C, the black panel temperature was 63^{o}C, and the irradiance was 0.35 w/m^2. The treatment cycle was 102 minutes of light followed by 18 minutes of light and water spray.

RESULTS AND DISCUSSION

All-aliphatic polyurea coatings demonstrate superior gloss and color-stability; but as noted in the introduction, this increased stability does not necessarily carry over into the mechanical properties of the coating. In addition, although an aliphatic amine is much more stable to air oxidation than its aromatic counterpart, it can slowly yellow over time, and some additives are capable of accelerating this effect.

In consultation with Ciba Specialty Chemicals Corp., nine different UV stabilizers were evaluated for their ability to enhance both the color and mechanical properties retention (inferred from crack resistance) of a typical polyurea coating. The standard formulation (without stabilizer) used is shown in Table 2. Although Clearlink 1000 is often blended with IPDA, Clearlink 1000 was used as the sole curative in order to minimize component effects on the coating. The physical properties shown were determined after two weeks and are for the formulation containing no stabilizer. Adding stabilizers led to no significant physical property changes at ambient conditions.

Effect of the Stabilizers on Yellowing

The nine stabilizers that were evaluated are proprietary materials from Ciba Specialty Chemicals Corp. and are referred to only by letters. These letters are also used to identify the formulations. The stabilizer level was 0.75% (by weight) of the total formulation in all cases. The control formulation (no stabilizer) is denoted as "None". Color stability was followed as a function of time using the procedure outlined in the experimental section. The aliphatic coating specimens were evaluated after 100, 1015, 2127, and 3015 hours, and the results are summarized in Table 3 and Figure 1. A standard white

Table 2. General Formulation for the Aliphatic Polyurea Stability Study.

Components/Properties	Static Mixing
A-Side	
Desmodur I (%)	45.8
JEFFAMINE D-2000 (%)	54.2
% NCO	15.0
Index	105
B-Side	
JEFFAMINE D-2000 (%)	48.0
Clearlink 1000 (%)	52.0
Stabilizer (%)	(1.6)
Volume Ratio (A/B)	1.00
Weight Ratio (A/B)	1.09
Spray/Cartridge Temp. (C)	23
Coating Thickness (mil)	31
Pot Life (sec)	~ 15
Tack-free Time (min)	9.0
Hardness, instant (Shore D)	55
After 10 sec (Shore D)	47
Tensile Strength (psi)	3540
100% Modulus (psi)	1750
300% Modulus (psi)	1920
Elongation (%)	490
Tear Resistance (pli)	630
Tear Prop. Resist. (pli)	540
Resilience, Bashore (%)	42

The amount of each component in the formulation is expressed as a percentage of either the A-side or the B-side. * The stabilizer made up 0.75% of the total formulation by weight.

back up tile had a yellowing index (YI) of 8.7, which is shown as a heavy line in the figure. The ten coatings had initial YI values between 9.6 and 10.6 and appeared clear and colorless.

All of the coatings slowly increased in color, as illustrated in Photograph 1, but even after 3000 hours the highest YI was just 12.9 (Formulation A is denoted as Ali A). It is important to note that what may appear to be coloration of some samples at time 0 is due to the lighting conditions at the time of the photography. Three of the formulations (those containing stabilizers A, E, and F) resisted cracking for more than 2500 hours in the weatherometer. The control coating developed a crack after about 100 hours and was removed from the chamber. This cracking is consistent with the earlier results of Rek et al. [3].

To help put the slight increase in color observed for the aliphatic coatings into perspective, a series of aromatic coatings were prepared using Rubinate 9495 (an MDI-based quasi prepolymer), JEFFAMINE D-2000, Unilink 4200, and DETDA. A general formulation using one of the stabilizers is shown in Table 4. In the aromatic coatings study, the three best stabilizers from the aliphatic study were evaluated as well as one formation containing both Stabilizer F and TiO_2 at a level of 8% of the total formulation.

As expected, the initial YI of the aromatic control was much higher than the aliphatic control (40 compared to 9.6) as noted in Table 5. Figure 2 shows the results of the three best aliphatic coatings (Ali) and the corresponding aromatic coatings (Aro) as a function of time in the weatherometer. The ability of the aliphatic coatings to resist yellowing is far superior to the aromatic coatings using the same amount of stabilizer. This is dramatically illustrated in Photograph 2, which shows the weatherometer specimens for the aliphatic and aromatic formulations that were both stabilized with the same amount of Stabilizer F.

Although the stabilizers did initially retard yellowing of the aromatic coatings, their color values still doubled within about 200 hours. The best result for the aromatic coatings was observed for the formulation incorporating Stabilizer F and 8% TiO_2 (Aro F-TiO_2). This opaque white coating had a color between 59 and 71 YI, and it showed obvious yellowing after 200 hours. Photograph 3 shows the test specimens for all of the aromatic coatings.

Table 3. Color Stability as a Function of Time for the Aliphatic Formulations.

	Hours After XAW (Spray, 63°C) Exposure				
Stabilizer	0	100	1015	2127	3015
None	9.6	9.5	*		
A	10.6	10.4	11.3	11.7	12.9
B	9.9	10.3	10.8	11.6	*
C	9.6	9.6	9.8	10.3	*
D	9.8	9.7	9.5	10.6	*
E	10.2	9.9	10.8	11.0	11.9
F	9.9	9.9	11.8	11.4	12.1
G	10.2	10.1	10.6	11.1	*
H	10.0	10.1	10.7	11.4	*
I	10.1	11.6	11.2	12.5	*

* Sample developed cracks.

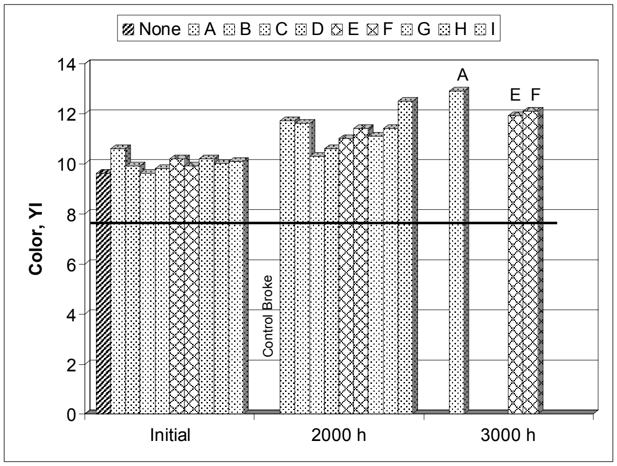
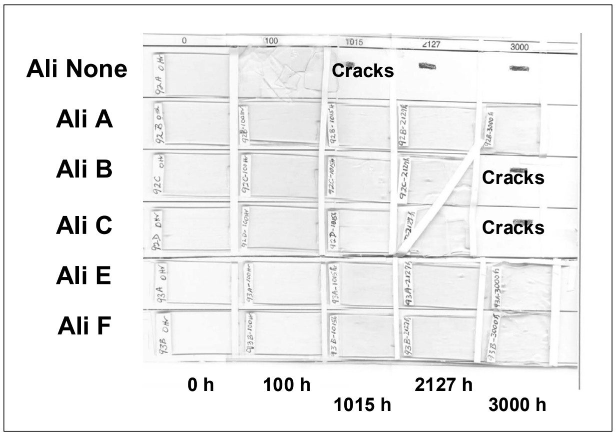


Figure 1. *Color Stability of the Aliphatic Polyurea Coatings Based on Clearlink 1000 with Ciba Stabilizers.*



Photograph 1. *Weatherometer Testing of the Aliphatic Coatings.*

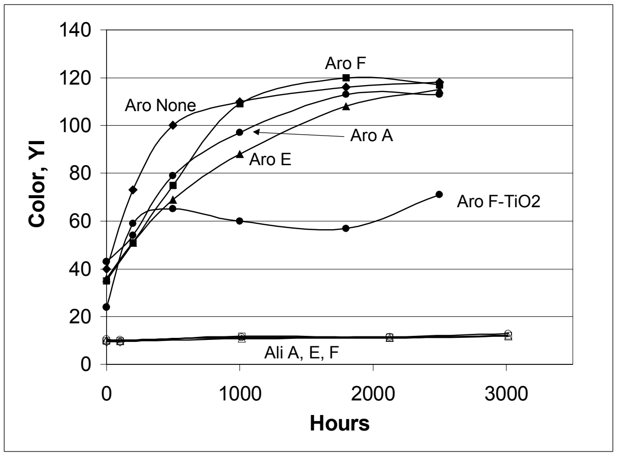
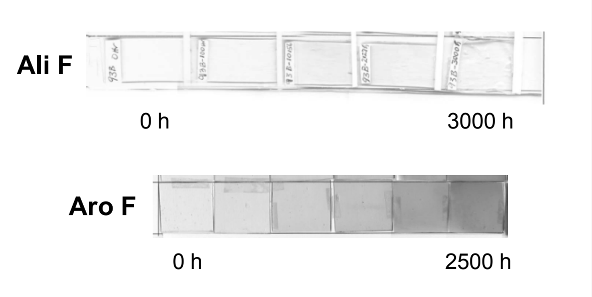


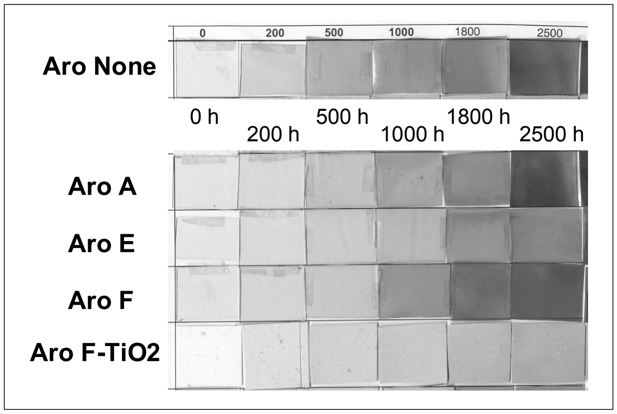
Figure 2. *Color Stability of the Aliphatic versus the Aromatic Polyurea Coatings.*

Table 4. General Formulation for the Aromatic Polyurea Stability Study.

A-Side	
Rubinate 9495 (%)	100.0
% NCO	15.2
Index	105
B-Side	
JEFFAMINE D-2000 (%)	54.8
Unilink 4200 (%)	31.5
DETDA (%)	12.1
Stabilizer (%)	1.6
Volume Ratio (A/B)	1.00
Weight Ratio (A/B)	1.14
Coating Thickness (mil)	30
Pot Life (sec)	< 20
Tack-free Time (min)	21
Hardness, instant (Shore D)	49
After 10 sec (Shore D)	41
The stabilizer made up 0.75% of the total formulation by weight.	



Photograph 2. *Yellowing Comparison of the Aliphatic and Aromatic Coatings Incorporating Stabilizer F.*



Photograph 3. *Weatherometer Testing of the Aromatic Coatings.*

Table 5. Color Stability as a Function of Time for the Aromatic Formulations.

	Hours After XAW (Spray, 63°C) Exposure					
Stabilizer	0	200	500	1000	1800	2500
None	40	73	100	110	116	118
A	43	54	79	97	113	113
E	36	51	69	88	108	115
F	35	51	75	109	120	117
F-TiO_2	24	59	65	60	57	71

None of the aromatic samples showed any cracks after 2500 hours exposure.

Effect of the Stabilizers on Crack Resistance

The crack resistance of the coatings tested in the weatherometer was determined by simple visual inspection. The aliphatic coating without stabilizer (the control) successfully resisted yellowing in the harsh weatherometer regime; however, it showed significant cracking after 100 hours. The severity of the cracking in the control specimen prohibited us from estimating how much the stabilizers might have retarded the slight yellowing observed in the aliphatic samples. The extent of the crack development in the control specimen would most likely have led to coating failure in an application where the time of exposure corresponded to the accelerated aging in the weatherometer.

The effect that the various stabilizers had on crack resistance differed significantly in the aliphatic coatings. As illustrated in Figure 3 and tabulated in Table 6, Stabilizer I was completely ineffective at improving crack resistance. Stabilizer D increased crack resistance about 10-fold to 1000 hours, and Stabilizers B, C, G, and H increased crack resistance up to about 2000 hours. The three best stabilizers (A, E, and F) actually improved crack resistance by 30-fold up to about 3000 hours. Of the three best performers, we would recommend Stabilizer F. This liquid additive can be obtained from Ciba Specialty Chemicals Corp. by asking for Stabilizer F.

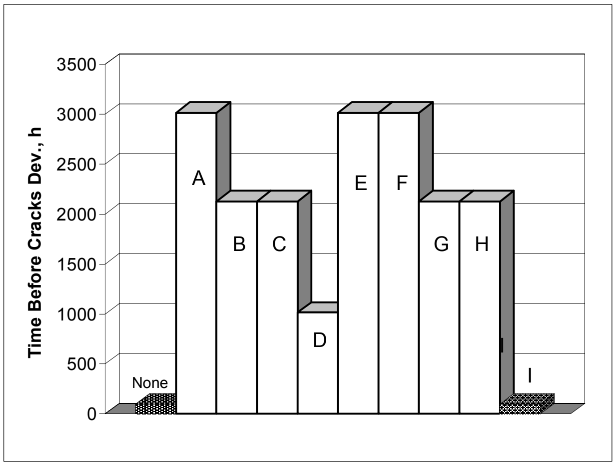


***Figure 3.** Crack Resistance of Polyurea Coatings Based on Clearlink 1000 with Ciba Stabilizers.*

Table 6. Crack Resistance as a Function of Time.

	Hours After XAW (Spray, 63°C) Exposure			
Stabilizer	100	1015	2127	2500
None	cracks	--	--	--
A	good	good	good	**good**
B	good	good	cracks	--
C	good	good	cracks	--
D	good	cracks	--	--
E	good	good	good	**good**
F	good	good	good	**good**
G	good	good	cracks	--
H	good	good	cracks	--
I	cracks	--	--	--

CONCLUSION

It is well known that aliphatic polyurea coatings are much more resistant to yellowing, are more color stable, and retain gloss much better than their aromatic counterparts, but the retention of the mechanical properties over time is just as important. In accelerated aging tests using a xenon lamp weatherometer, we have shown that the use of certain UV stabilizers can dramatically improve the crack resistance of aliphatic polyurea coatings, and therefore, the retention of their mechanical properties. In the best case, crack resistance improved 30-fold (up to 3000 hours) by adding just 0.75% (by weight) of the right stabilizer. The selection of a suitable stabilizer package will, naturally, depend upon the formulation and its application.

Although photoinitiated radical attack on the aromatic groups causes the aromatic coatings to yellow significantly, this "radical scavenging" appears to help protect the integrity of the polymer backbone. In a future report, we hope to present more complete data that will compare the mechanical (strength) properties of the aliphatic and aromatic coatings as a function of weatherometer exposure.

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BIOGRAPHIES

David W. House

David W. House, Ph.D., is currently an independent consultant. He received his bachelor's degree in chemistry from the University of North Carolina at Charlotte in 1973 and his doctorate in organic chemistry from the University of Illinois (Urbana-Champaign) in 1978. He joined UOP LLC in 1978 where he worked in research and development until 2002. He began working in polyurethanes in 1983 and in 1985, he started directing the research and development and the technical service support for both cellular and noncellular applications. In addition, his work included the investigation and development of novel components for polyurethanes and polyureas, during which he co-invented the Unilink and Clearlink brands of diamine curatives.

Dr. house has also been involved with the use of molecular sieves as additives in polymers and with heterogeneous catalysis to carry out organic syntheses. Previous work covers the development of a new series of electrically conducting polymers, a method for the large-scale diastereomeric separation of optical isomers of aminoacids and alcohols, the design of new chiral stationary phases for the liquid chromatographic separation of optical isomers, and the desulfurization of gasoline.

Dr. House is a member of Sigma Xi, the American Chemical Society, and the Organic Chemistry Division of the American Chemical Society. He is the author or co-author of 46 U.S. patents, more than 35 scientific papers, and numerous technical presentations at professional societies.

Ray V. Scott, Jr.

Ray Scott is currently President of PolyTechnologies, Inc. The new firm, which was founded March 1, 2002, is part of a strategic alliance with companies such as UOP LLC and BASF to offer full service sales to customers including consulting, toll manufacturing and blending, contract research capabilities, and specialized sourcing for limited specialty chemicals.

Prior to forming PolyTechnologies, Inc., Ray was the Business Manager of the Plastics Additives business at UOP LLC, where he was a co-founder of the Unilink and Clearlink brands of diamines. Ray has been active in the polyurethane and polyurea area for over 25 years and has authored or co-authored over 35 technical presentations.

Ray holds 20 U.S. patents in the fields of polyurethanes and polyurea.

Before joining UOP in 1980, Ray held various sales and sales management positions with Air Products and Chemicals and with Goodyear Tire and Rubber Co. Ray received his bachelor's degree in Chemical Engineering from N. C. State University and an MBA from Keller Graduate School of Management. Ray is active in the Commercial Development and Management Association, having served as President in 1993, and received their Golden "C" award in 1989 recognizing his achievements in commercial development. Ray is also active in the Polyurea Development Association and will serve as President in 2003.

John F. Leon

John Leon currently works as Manager, Plastic Additives Business in the Adsorbents and Specialties Group of UOP LLC based in Des Plaines, Illinois. John is responsible for both direct sales and sales through distributors in North America. He received his bachelor's degree in biology from Carthage College in 1987. John joined UOP LLC in 1988 and held numerous positions in research until he joined the Adsorbents and Specialties Group in 1998. John was recently elected to the Board of Directors of the Polyurea Development Association for the term 2003-2005.