New Epoxy/Anhydride Chemistry for Durable, High Solids Coatings

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INTRODUCTION

Heightened concern for the environment across many segments of America has led to increasingly stringent regulations regarding the use of volatile organic compounds (VOC) in coatings, cleaning solutions, adhesives and sealants, refrigerants and fuels[1]. Embodiment of this concern has taken forms as diverse as comprehensive governmental regulations and increased consumer demand for products produced by "green" technologies. Probably the most pervasive of regulations are the Clean Air Act Amendments of 1990 which have brought about major changes in approaches to formulation and application of coatings, among other things.

A survey of trade literature and technical journals in recent years suggests that changes in technology to accommodate lower VOC coating formulations have been rapid and effective. However, in the manufacturing and service sectors of US industry the high cost of capital, high potential product liability and general concern for customer satisfaction comprise a formidable inertia to change coating systems unless there is absolutely no choice in a given situation. Today's regulatory climate provides a powerful economic stimulus to implement new, compliant technologies.

OEM Automotive Coatings

Automotive manufacturing in North America is a microcosm of the general coatings industry. Auto OEMs have their own particular material and capital cost constraints to work within, but in terms of performance, they have the strictest requirements of any segment of the weatherable/durable coatings industry. Coatings which will satisfy automobile manufacturers will likely meet or exceed the performance expectations of all other segments provided that the coating chemistry is applicable to those other segments.

Automotive coatings technologies have undergone substantial change in the last twenty years and will likely see even further change shortly before the turn of the century. A significant shift in performance focus has occurred in the last decade due to increasing liability concerns associated with "environmental etch" -- the physical erosion of coating material on vehicles exposed to acid rain. While acrylic melamine chemistry continues to enjoy favored status in terms of overall material volume applied on North American automobiles, it has become the target chemistry for improvement or replacement by new, "etch-resistant" coating systems in topcoat applications. These new systems present opportunities for suppliers to participate in providing coating systems, raw materials and equipment to manufacturers for future generations of vehicles.

The most prominent recent trend, considering both performance and regulatory factors, is to utilize "high solids" (3.5 lbs VOC/gallon or less) coating systems. For instance, a low VOC electrocoat primer might be followed by a waterborne or powder primer surfacer. Basecoat may be either waterborne or solventborne. The clearcoat, which provides the smoothness, depth and luster to the vehicle can then be applied as a medium to high solids solventborne system with traditional equipment. With this integrated systems approach, total VOCs in pounds per manufacturing site can be controlled by careful production scheduling.

Increasingly strict regulatory requirements will stimulate the evolution of automotive coatings technology in the near future[2]. Technical strategies to meet the demands of lower site emissions include:

1) abatement of emissions "at the stack" after application on the paint line[3]
2) wider implementation of novel application technologies like supercritical CO_2 spray[4]
3) increasing use of non-volatile reactive solvents
4) increasing use of waterborne coatings
5) increasing use of powder coatings
6) reduction in molecular weight/viscosity of coating resins to afford higher solids

Implicit in these strategies are advantages and limitations that will ultimately drive one approach further than the rest as the "best available technology". Strategy one is probably the least attractive due to high capital equipment costs and tax considerations, and general preference for source reduction strategies upstream of the abatement option[5,6]. Strategies two through five will likely produce one dominant driver at some point in the future.

For the present, that leaves strategy six as the most likely area in which immediate coatings system improvements will be made. These improvements will necessarily comprise more than just incremental performance enhancements; cost and product stewardship concerns will be critical factors which must be considered during the research and development phases of new materials.

DURABLE, HIGH-SOLIDS SOLVENTBORNE COATINGS

The following discussion focuses on the application of novel technology to category six -- higher solids solventborne systems via reduced molecular weight/viscosity of system components.

High solids solventborne epoxy/acid and epoxy/anhydride systems for automotive clearcoats began to appear in the literature in the mid to late 80s[7,8]. While there was some established history for the use of "epoxy/carboxy" chemistries in durable coatings applications, this was nonetheless an unexpected challenge to the perceived preeminence of polyurethane chemistry and was especially significant in light of the common perception that epoxy resins (i.e., aromatic glycidyl ethers) don't "weather" well.

Traditional applications of epoxy/acid chemistry in durable coatings include systems as diverse as multifunctional epoxies reacted with dicarboxylic acids, multifunctional (alkyl) acrylic acids reacted with difunctional epoxies and multifunctional (alkyl) acrylic epoxies reacted with multifunctional carboxylic acids[9]. Principal advantages of epoxy/acid chemistry include low raw material cost, excellent film appearance, durability and environmental etch resistance[10]. In addition, the chemistry is versatile enough to produce ambient or elevated temperature cure with common catalysts. Epoxy/acid systems can be applied as solventborne, powder or waterborne coatings.

Traditional applications of epoxy/anhydride chemistry are somewhat more limited. Typical anhydride resins used in durable coatings are comprised of polymers based on maleic or itaconic anhydrides[11]. These are commonly crosslinked by difunctional epoxy resins, multifunctional (alkyl) acrylic epoxies or both. Some references are made to lower molecular weight compounds such as methyl hexahydrophthalic anhydride (MHHPA) being used to crosslink multifunctional epoxies[9, 12], but concerns about the pulmonary toxicity of these materials limits their efficacy in spray applications.

In each of the above cases, the anhydride moiety is a five-membered cyclic structure:

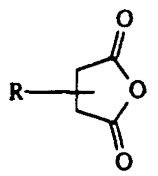

Figure 1. Five-membered cyclic anhydride

However, other permutations of the anhydride linkage are possible; poly alkyl poly anhydrides (e.g., poly adipic poly anhydride) are anhydride-"bridged" linear polymers which can react in the presence of strong nucleophiles to produce polyesters and/or polyamides, for instance.

Another distinct example of the anhydride functional group is a linear linkage as described above, but with one end pendant to a larger structure such as a polymer or oligomer "backbone". Such structures, insofar as their utilization in coatings, were unreported until recently[13, 14]. This paper deals with some of the features of materials which contain linear pendant anhydride (LPA) moieties.

Linear Pendant Anhydrides (LPA)

The simplest representation of this class of materials is seen in Figure 2: the anhydride linkage is terminated by a simple alkyl group (R') on one side, and attached to a central moiety or backbone (R) on the other.

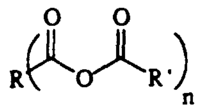

Figure 2. Generic linear pendant anhydride (LPA)

The nature of LPA resins is substantially affected by the structures of R and R' and can be specifically tailored to meet desired performance criteria. For instance, where R is a polymeric backbone, high Tg, high-melting friable solids are easily isolated from process solvents. By contrast, where R is a multifunctional polyester oligomer, lower Tg, low-melting solids can be isolated.

Where R' is methyl, cure with epoxy resins and suitable catalysts can be realized at ambient to bake temperatures; where R' is a higher order residue, such as an isobutyl or t-butyl group, cure is difficult even during extended bake times at high temperatures. LPA resins terminated with substituted alkyl groups can be formulated to stable one-package coatings; partially acylated LPA resins have very high reactivity and relatively short pot lives when formulated as single-package coatings.

FORMULATION AND APPLICATION OF LPA-BASED COATINGS

The following examples comprise actual formulations with spray viscosities, application parameters and coatings evaluation data. A thorough description of each system is included for purposes of illustrating the wide range of binders/crosslinkers which can be utilized.

Additives to the fully formulated systems were based on weight percentages of total resin solids (TRS). Equivalent weights are expressed on a solution basis. All formulations included Tinuvin® 292 hindered amine light stabilizer (HALS) at 1%, Tinuvin® 384 ultraviolet absorber (UVA) at 1.5%, BYK 358 flow control agent at roughly 0.1% and phosphonium catalyst at 2%. Each formulation was "let down" to spray viscosity (35 +/- 1 Zahn #2 seconds) with Dowanol® PMA.

Formulations were spay-applied through a standard siphon-feed pneumatic spray gun to bare polished steel or waterborne basecoat on electrocoated steel. Typical spray parameters were 70 psi line pressure, 6 psi cup pressure. Panels were "flash dried" for 5-10 minutes and then baked at 265-285 deg. F in a forced-air oven for 30 minutes. Physical properties were typically measured within twenty-four hours after bake.

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Each formulation was measured for actual solids (ASTM D-2369) and contrasted with theory. Discussion of that particular measurement follows the formulation and performance inventory for systems I-VI. Other performance parameters of interest included 20 degree gloss over basecoat, DOI (distinctness of image), Knoop Hardness and Gardner Impact resistance. A brief discussion of durability performance also follows the next section.

Formulation I: LPA Copolymer and Difunctional Glycidyl Ester

The LPA binder was the acetylated product of a 25% (w/w) methacrylic acid copolymer, with a balance of acrylic co-monomers and styrene. Diglycidyl-1, 2-cyclohexane dicarboxylate, a low viscosity liquid epoxy resin, was utilized at 100% solids as the crosslinker.

Component	Weight (g)
Anhydride Binder Resin (66.3% solids; 867 FEW*, solution)	80.0
Diglycidyl-1,2-cyclohexane dicarboxylate (159 EEW*)	25.7
Tetraphenyl phosphonium bromide (30% solution)	5.25
Tinuvin 292	0.79
Tinuvin 384	1.18
BYK 358	0.16
Dowanol PMA	38.6
Theoretical system solids = 54.3%	
Measured system solids = 52.8% +/- 1.2	
Zahn #2 time = 35.3 seconds. Bake 30 minutes at 265 deg. F	
Film Thickness	2.69 +/- 0.09 mils
MEK Resistance (# double rubs to failure)	200+
Gloss (20 degree over basecoat)	84 +/- 1
Distinctness of Image	90 +/- 2
Knoop Hardness	2.9 +/- 0.10
5% NaOH (24 hour spot test)	Pass (no staining or spotting)
10% H2SO4 (24 hour spot test)	Pass
Gardner Impact (steel only)	80 in-lb forward
	20 in-lb reverse

*FEW = Functional Equivalent Weight; EEW = Epoxide Equivalent Weight

Formulation II: Tetrafunctional LPA Oligomer and GMA Copolymer

The GMA copolymer binder was based on 40% (w/w) glycidyl methacrylate "loading" in the monomer feed with a balance of acrylic co-monomers and styrene. The theoretical Tg of the GMA copolymer [Fox method[15]] was calculated to be 34 deg. C. The measured Tg [DSC method] was 36.6 deg. C. The LPA oligomer was the acetylated product of pentaerythritol reacted with a 50/50 weight blend of MHHPA/HHPA.

Component	Weight (g)
GMA Copolymer Binder Resin (63.9% solids; 534 EEW)	85.3
Tetrafunctional LPA Oligomer (81.0% solids; 340 FEW)	50.0
Tetraphenyl phosphonium bromide (30% solution)	6.33
Tinuvin 292	0.95
Tinuvin 384	1.42
BYK 358	0.19
Dowanol PMA	31.3
Theoretical system solids = 56.6%	
Measured system solids = 54.8% +/- 0.2	
Zahn #2 time = 34.9 seconds. Bake 30 minutes at 265 deg. F	
Film Thickness	2.86 +/- 0.17 mils
MEK Resistance (# double rubs to failure)	200+
Gloss (20 degree over basecoat)	84 +/- 1
Distinctness of Image	92 +/- 2
Knoop Hardness	7.32 +/- 0.62
5% NaOH (24 hour spot test)	Pass
10% H2SO4 (24 hour spot test)	Pass
Gardner Impact (steel only)	60 in-lb forward
	10 in-lb reverse

Formulation III: Trifunctional / Tetrafunctional LPA Oligomer and GMA Copolymer

The GMA copolymer binder used was as described in Formulation II. The LPA oligomer was the acetylated product of a 50/50 weight blend of trimethylolpropane and pentaerythritol reacted with a 50/50 weight blend of MHHPA/HHPA.

Component	Weight (g)
GMA Copolymer Binder (63.9% solids; 534 EEW)	84.8
LPA Oligomer Blend (71.9% solids; 413 FEW)	60.0
Tetraphenyl phosphonium bromide (30% solution)	6.49
Tinuvin 292	0.97
Tinuvin 384	1.46
BYK 358	0.20
Dowanol PMA	16.6
Theoretical system solids = 59.7%	
Measured system solids = 57.9% +/- 0.4	
Zahn #2 time = 34.7 seconds. Bake 30 minutes at 265 deg. F	
Film Thickness	2.88 +/- 0.13 mils
MEK Resistance (# double rubs)	200+
Gloss (20 degree over basecoat)	84+/- 1
Distinctness of Image	92 +/- 2
Knoop Hardness	10.5 +/- 0.36
5% NaOH (24 hour spot test)	Pass
10% H2SO4 (24 hour spot test)	Pass
Gardner Impact (steel only)	60 in-lb forward
	10 in-lb reverse

Formulation IV: Difunctional LPA Oligomer and GMA Copolymer

The GMA copolymer binder used was as described in Formulation II. The LPA oligomer was the acetylated product of neopentyl glycol reacted with a 50/50 weight blend of MHHPA/HHPA.

Component	Weight (g)
GMA Copolymer Binder (63.9% solids; 534 EEW)	79.9
Difunctional LPA Oligomer (81.6% solids; 412 FEW, solution)	50.0
Tetraphenyl phosphonium bromide (30% solution)	6.12
Tinuvin 292	0.92
Tinuvin 384	1.38
BYK 358	0.18
Dowanol PMA	5.9
Theoretical system solids = 66.5%	
Measured system solids = 62.5% +/- 0.3	
Zahn #2 time = 33.8 seconds. Bake 30 minutes at 265 deg. F	
Film Thickness	2.84 +/- 0.29 mils
MEK Resistance (# double rubs to failure)	100
Gloss (20 degree over basecoat)	83 +/- 1
Distinctness of Image	94 +/- 2
Knoop Hardness	6.49 +/- 0.26
5% NaOH (24 hour spot test)	Pass
10% H2SO4 (24 hour spot test)	Pass
Gardner Impact (steel only)	40 in-lb forward
	<5 in-lb reverse

Formulation V: Tetrafunctional LPA Oligomer and Difunctional Glycidyl Ester

The glycidyl ester crosslinker was defined in experimental formulation I. The LPA oligomer was the acetylated product of pentaerythritol reacted with a 50/50 weight blend of MHHPA/HHPA.

Component	Weight (g)
Tetrafunctional LPA Oligomer (81.0% solids; 340 FEW)	70.0
Diglycidyl-1,2-cyclohexane dicarboxylate (159 EEW)	35.5
Tetraphenyl phosphonium bromide (30% solution)	6.15
Tinuvin 292	0.92
Tinuvin 384	1.38
BYK 358	0.18
Dowanol PMA	36.1
Theoretical system solids = 64.2%	
Measured system solids = 63.9% +/- 0.5	
Zahn #2 time = 34.6 seconds. Bake 30 minutes at 285 deg. F	
Film Thickness	2.83 +/- 0.23 mils
MEK Resistance (# double rubs to failure)	200+
Gloss (20 degree over basecoat)	82 +/- 1
Distinctness of Image	80 +/- 2
Knoop Hardness	8.13 +/- 0.70
5% NaOH (24 hour spot test)	Pass
10% H2SO4 (24 hour spot test)	Pass
Gardner Impact (steel only)	40 in-lb forward
	<5 in-lb reverse

Formulation VI: Trifunctional / Tetrafunctional LPA Oligomer and Difunctional Glycidyl Ester

The glycidyl ester crosslinker was defined in experimental formulation I. The LPA oligomer was the acetylated product of a 50/50 weight blend of trimethylolpropane and pentaerythritol reacted with a 50/50 weight blend of MHHPA/HHPA.

Component	Weight (g)
LPA Oligomer Blend (71.9% solids; 413 FEW)	70.0
Diglycidyl-1,2-cyclohexane dicarboxylate (159 EEW)	37.3
Tetraphenyl phosphonium bromide (30% solution)	5.84
Tinuvin 292	0.88
Tinuvin 384	1.13
BYK 358	0.18
Dowanol PMA	13.6
Theoretical system solids = 71.0%	
Measured system solids = 69.9% +/- 0.2	
Zahn #2 time = 35.2 seconds. Bake 30 minutes at 285 deg. F	
Film Thickness	1.85 +/- 0.08 mils
MEK Resistance (# double rubs to failure)	200+
Gloss (20 degree over basecoat)	83 +/- 1
Distinctness of Image	91 +/- 2
Knoop Hardness	6.59 +/- 0.76
5% NaOH (24 hour spot test)	Pass
10% H2SO4 (24 hour spot test)	Pass
Gardner Impact (steel only)	60 in-lb forward
	<5 in-lb reverse

RESULTS AND DISCUSSION

The principal objective of contrasting the previous six experimental formulations was to demonstrate the versatility in enhancing theoretical system solids by making subtle changes in the architecture of the constituent binder and crosslinker resins. LPA resins are inherently simple to design; the ultimate performance goal of a coating system should be achievable by simple experimentation with different LPA structures. Where very high solids (<2.6 lbs VOC/gal) are desired, and where high crosslink density can be tolerated, a system such as experimental formulation #6 is feasible. Where a softer, more flexible coating formulation is desired, and where higher VOC levels can be tolerated, a system such as experimental formulation #1 is indicated.

Table I summarizes the six experimental systems, and a "standard" polyester polyol / HDI trimer polyurethane system from the perspective of formulation solids at roughly comparable viscosity. The systems are rank-ordered from lowest solids to highest solids, with no other performance parameters considered. Numbers in parentheses under System / Description indicate the theoretical functionality of the LPA oligomer(s).

Table I. Rank-Order of Experimental Formulated Systems by Theoretical Solids

System / Description	**Zahn #2 Viscosity (sec.)**	**Theoretical Solids (% w/w)**	**Measured Solids (% w/w)**
#1 - LPA Polymer / diglycidyl ester	35.3	54.3	52.8 +/- 1.2
"Standard" - Polyester polyol / HDI Trimer Polyurethane	34.3	54.9	54.8 +/- 0.0
#2 - LPA Oligomer (4) / 40% GMA Copolymer	34.9	56.6	54.8 +/- 0.2
#3 - LPA Oligomer (3 + 4) / 40% GMA Copolymer	34.7	59.7	57.9 +/- 0.4
#5 - LPA Oligomer (4) / diglycidyl ester	34.6	64.2	63.9 +/- 0.5
#4 - LPA Oligomer (2) / 40% GMA Copolymer	33.8	66.5	62.5 +/- 0.3
#6 - LPA Oligomer (3 + 4) / diglycidyl ester	35.2	71.0	69.9 +/- 0.2

With concern for VOCs in coating formulations being a primary driver for new technology development, the delta between theoretical and actual (measured) solids in the experimental systems deserves some attention. In effect, there are two primary forces at work which lead to a loss of some of the system "solids": 1) volatility of the constituents and 2) self-condensation of LPA functional groups to form an intermolecular linkage and liberate a volatile symmetrical anhydride. Both phenomena lead to an undesirable increase in measured VOC and are related to the degree that each exacerbates the other.

In formulations such as #1, #2, #3 and #4 where one of the constituents is a polymer, fast vitrification of the film leads to a higher probability of unreacted low molecular weight material vaporizing from the matrix. This is nicely contrasted in formulations #1 and #4 where each system has a two-functional component. System #4 in particular loses 4% of its theoretical solids due to the loss of the volatile two-functional LPA molecule. System #1 utilizes a less volatile two-functional diglycidyl ester, which nonetheless will volatilize when tested alone by ASTM D-2369.

In the second situation described previously, the LPA functional group can condense with itself to liberate a volatile symmetrical anhydride, acetic anhydride (III) in the cases of the resins formulated for this study:

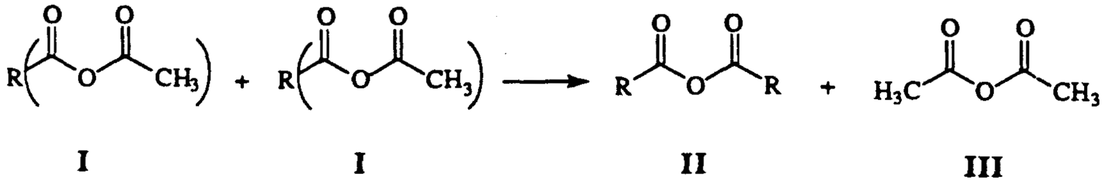

Figure 3. Self-condensation of LPA molecules.

It is not clear at present how the kinetics of this reaction relate to the desired reaction (LPA addition to oxirane); further studies should elucidate these differing features. For the present, it has been established that higher catalyst levels minimize the delta between theoretical and measured solids.

In systems which are lower in net functionality (formulations #5 and #6) due to the absence of polymeric constituents, better mixing and thus distribution of reactive moieties is possible. However, lower molecular weight equates to higher volatility and higher functional group loadings. The net result of this is a high "attrition potential" of acetic anhydride (III) from systems #5 and #6. 13.5% and 10.0% of these systems could be lost, theoretically, if the reaction depicted in Figure 3 were the predominant reaction rather than addition of LPA to oxirane.

As self-condensation progresses system stoichiometry becomes unbalanced, again leading to a higher probability of unreacted low molecular weight material (diglycidyl ester in this case) vaporizing from the matrix. The fractional deltas determined experimentally for these two systems (0.3 and 1.1%, respectively) suggests that self-condensation is a minor deficiency of this chemistry that can likely be overcome by system optimization, primarily as it relates to catalysis.

Other properties measured in this study suggest that coatings based on LPA and epoxy will fulfill typical requirements for high performance coatings, i.e., excellent appearance (gloss and DOI), solvent resistance and flexibility (extrapolated from Gardner Impact). No optimization of these experimental formulations was attempted for this study.

DURABILITY

One of the key required features for automotive coatings is durability -- the resistance of such coatings to environmental attack, including sunlight (UV radiation), oxygen, heat and moisture cycling, acid rain, bird and bug droppings, tree sap, etc. Current expectations for OEM automotive coatings in particular are that they will maintain both physical integrity and excellent appearance for the normal service life of the vehicle.

In the present study, durability testing requiring extensive investment of time was not possible. However, Figure 2 represents accelerated durability testing by QUV® 313b conducted in this laboratory for analogous formulations. The curves depicted in the graph represent average 20 degree gloss readings for six panels distributed randomly in two QUV cabinets. Error bars are not included, nor are the ordinate values expressed as percent retention of initial gloss, because the time to failure of these systems is substantially different from one another.

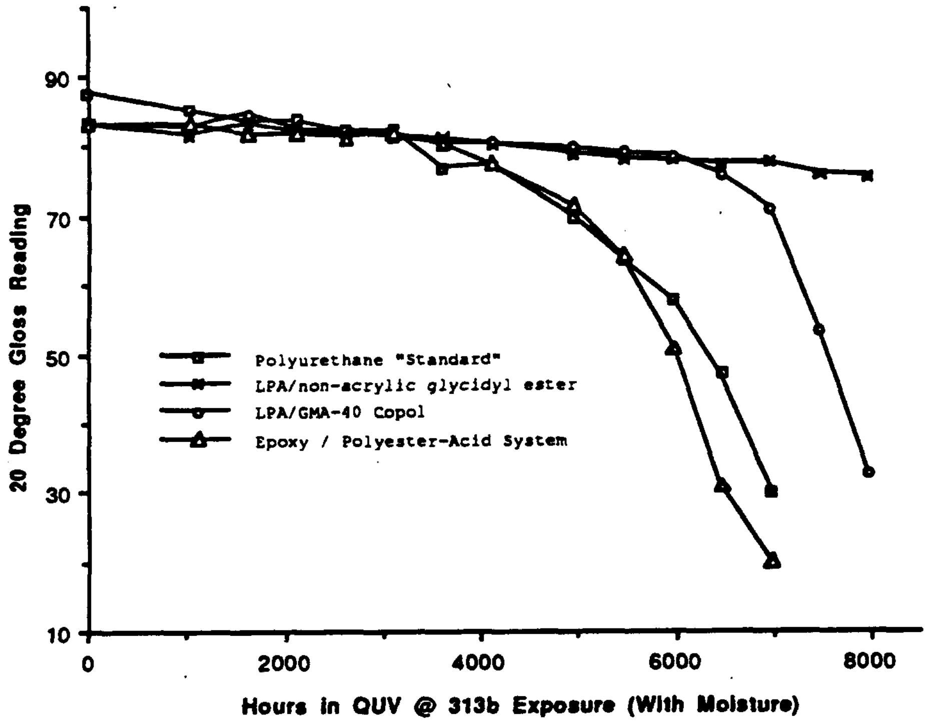

Figure 4. Gloss Retention of Epoxy / LPA Systems Versus "Standards" in QUV Testing

For the purposes of this study, four systems have been represented: 1) polyester polyol/ HDI trimer polyurethane "standard" [experimental system #7)], 2) LPA oligomer / glycidyl ester system [similar to experimental systems #5 and #6], 3) LPA oligomer / 40% GMA copolymer [experimental system #2] and 4) 40% GMA copolymer with saturated acid-functional polyester crosslinker. Each system was stabilized as reported for the experimental formulations in this study: 1% HALS and 1.5% UVA by weight based on total resin solids. The testing cycle was 4 h UV/60 deg. C, 4 h CON/50 deg. C as per ASTM D-4587.

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A cursory analysis of Figure 2 suggests that while "standard" polyester urethane and epoxy / acid clearcoat systems have excellent durability in this test to about 5000 hours exposure, the two LPA-based systems have even greater durability. System #2 was removed from the test condition after 9600 hours with over 70% retention of initial gloss. None of these test systems was optimized, although previous extensive experience with the polyurethane system led to its adoption as the "standard" for comparative purposes in this ongoing testing program.

CONCLUSIONS

In an effort to address the major driving forces for new technology development in durable coatings applications, a new epoxy-based chemistry was introduced. Performance standards for automotive coatings were chosen as a target in an evaluation of typical coating performance parameters including appearance, flexibility, solvent resistance and durability in accelerated laboratory testing. Perhaps the most important picture this study paints for the research community is that epoxy-based coatings, traditionally thought of as non-weatherable, are <u>very</u> durable while meeting all other requisite performance criteria.

Driving forces to lower VOC levels in paint systems while improving appearance, durability and reducing or minimizing cost will continue to force the evolution of new technologies. "Epoxy / carboxy" chemistry, one of the newest challengers in the marketplace, is substantially qualified to address these driving forces. In particular, linear pendant anhydride (LPA) / glycidyl ester technology offers tremendous latitude in binder / crosslinker architecture to address solids, flexibility and durability.

Very high solids formulations (< 2.6 lbs. VOC / gal) applicable to traditional application equipment are possible with this chemistry. Future work will explore alternative application methods for LPA-based systems. Exploration of system improvements will focus on laboratory evaluations of etch resistance and scratch / mar performance relative to standard paint systems.

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