Low VOC Carbamate Functional Coatings Compositions for Automotive Topcoats

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Polymers and oligomers having carbamate functional groups have been used in a variety of curable coating compositions. Carbamate functional polymers offer many advantages for automotive topcoats, such as outstanding resistance to environmental etching, scratching and marring, humidity, and UV exposure. Hydrophobic carbamate oligomers suitable for crosslinking with standard amino resins were synthesized and formulated into stable one-pack automotive clearcoats with low volatile organic compound (VOC) and excellent physical properties. Because of their unusually steep thermal viscosity curves, these oligomers are particularly adaptable to hot spray techniques that enable coatings in the 85-90% weight solids range to be applied with conventional electrostatic mini-bells.

INTRODUCTION

Many thermosetting coatings compositions have been tested to improve upon two fundamental issues with original equipment manufacturer's (OEM) automotive topcoat finishes: (1) susceptibility to a phenomenon known as "environmental etch" and (2) a vulnerability to car-wash gouges, grit, or other surface induced damage known as "scratch and mar." Environmental etch manifests itself as circular spots or erosion marks in the finish of a coating that cannot be polished or rubbed out. Three very important factors involved in etch are hydrolysis and mechanical stress due to water, chemical erosion from acid rain (particularly sulfuric acid), and the deposition of inorganic salts into the surface of the coating. The mechanical stress due to sudden spots of localized cooling on a paint film is very severe when the environmental factors include a light rainfall on very hot metal panels. At test sites in Jacksonville, FL, and in Phoenix, AZ, temperatures on black car hoods and panels in full sunlight have been measured at 196°F. Rain falling on cool panels has little or no effect. Field studies have shown that the etch damage caused by this stress was much more pronounced with coatings that have a low cured film glass transition temperature (T_g), as measured by dynamic mechanical analysis, than on those with a higher T_g.[1] It is theorized that lower T_g films have more free volume, are more porous, and become even more porous to the water as the panel surface temperature approaches the cured film T_g and are, thus, more susceptible to acid catalyzed hydrolysis. The role of particulate matter first reported by Wolff[2] has proven to be a major factor in etch. Inorganic particulate matter that has the ability to dissolve in water is especially damaging and serves as a focal point for subsequent episodes.[2] Much has been written about the role of hydrolysis of coatings films in environmental etch.[3-5] A representative laboratory comparison of the hydrolysis of ether linkages to the hydrolysis of urethane linkages has shown marked differences in ease of reaction, with the urethane being more than an order of magnitude slower. Extensive lab testing as well as many summers of Florida field testing has proven that hydrolysis is a major contributor to etching. Any crosslinks that are subject to acid catalyzed hydrolysis are potential sites for etch damage. Also, the importance of hydrolysis from an environmental point of view stems from the fact that upon introduction of a hydroxyl group into the parent molecule, chemicals are formed which are usually more susceptible to further attack through the process of biodegradation and photolysis.[6] The three primary contributors to etch are high temperature, moisture, and contaminants. The three prerequisites for improved etch are high T_g, hydrophobicity, and chemical resistance.

Scratch and mar damage to the finish of an automobile is a great deal more personally preventable than etch, since it usually occurs due to an act of man that can be prevented. Washing your car, whether at the car wash or

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Presented at the 27th Annual International Waterborne, High-Solids, and Powder Coatings Symposium, in New Orleans, LA, March 2000.

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in your driveway, is one of the most likely times it will get scratched. During in-plant repairing or polishing, driving through construction zones, parking in a crowded lot, or someone dragging their hand across the surface (especially if it contains a key) are other likely times when an automotive topcoat can get damaged or abraded.

In recent years, the scratch, mar, and abrasion resistance of automotive coatings has been extensively studied by both OEM coatings suppliers and auto manufacturers.[7-9] Much has been written about providing meaningful test methods that correlate to observed field damage as well as characterizing polymer systems and formulations that contribute the optimum physical properties needed to minimize damage.[10-13] The ability to quantify what the variances in coating attributes contribute to increased scratch resistance, however, remains a subject of controversy.[10] This paper will describe one type of model carbamate clearcoat that has shown very good gloss retention on the Crockmeter test (described in more detail later) for scratch and mar resistance.

The first comprehensive field etch studies were run in 12 U.S. cities in the summer of 1987 where it was found that Jacksonville's Blount Island was probably the most severe U.S. site for evaluating etch damage. Since then, environmental etch resistant coatings have been a top priority and their use has steadily increased in the automotive industry. Producing clearcoats with resistance to acid rain and other environmental pollutants has consumed significant amounts of clearcoat development resources for the last 14 years. Concurrently, for the past five to six years, much time and effort has been spent on improving the scratch and mar resistance of automotive clearcoats, all the while attempting to maintain or improve the volatile organic compound (VOC) to meet automotive plant permit compliance.

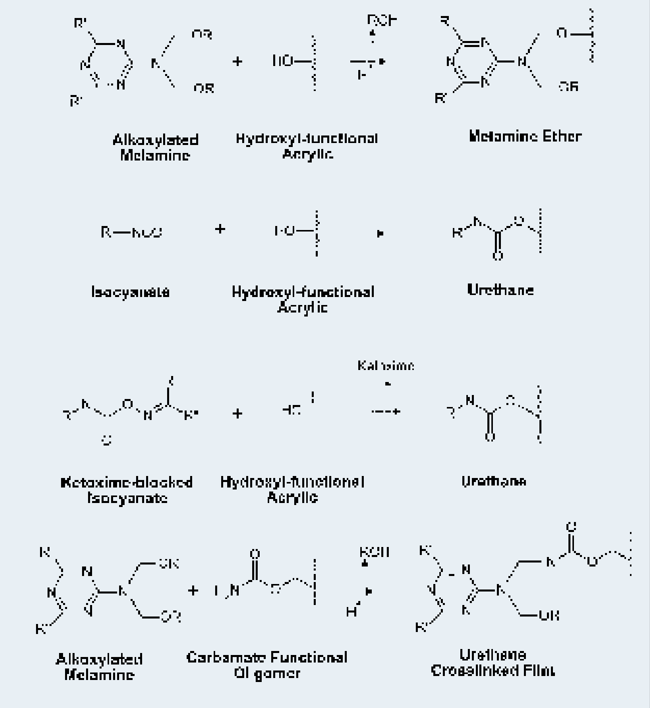


Figure 1—Crosslink comparison.

Environmental etch damage, along with scratch and mar, are significant elements in warranty considerations for manufacturers and, subsequently, for OEM coatings suppliers.[14] A number of various chemistries have been championed by different companies to improve both etch resistance and scratch and mar resistance. All of these technologies show some degree of improvement depending on whose surveys and which numbers you choose to look at. The good news for consumers is that the finish on your car today is far more environmentally etch resistant than it was 13 years ago due to major efforts by automotive coatings suppliers. Finishes, however, are not perfect, and continuous improvements are being made each year.

The standard chemistry for high-solids automotive clearcoats in 1987 was a hydroxyl functional acrylic polymer crosslinked with alkoxylated melamine. As can be seen in *Figure* 1, these systems depended on "ether" crosslinks, which were particularly susceptible to hydrolysis. Thus, the main disadvantage was poor resistance to acid rain and environmental fallout. It was well known early on that hydroxyl functional acrylic resins crosslinked with a polyisocyanate gave urethane crosslinks with much improved environmental etch resistance. Although some automotive assembly plants converted to this technology for high-end units, the disadvantages included higher cost, required two-component tooling, and weaker scratch and mar resistance. Concurrently, in the early 90s, development efforts were underway to convert to a one component clearcoat utilizing either blocked isocyanurates/acrylic polyol, epoxy/acid, epoxy/anhydride, or alkoxysilane chemistry. Some of the various disadvantages these systems needed to overcome included yellowing during baking, storage instability, inadequate chip resistance, toxicity, economics, poor mar resistance, inadequate appearance, brittleness, or intercoat adhesion failure to subsequent repair coats. The trend since 1995 has been to blend a combination of various crosslink chemistries in attempts to overcome some of these deficiencies

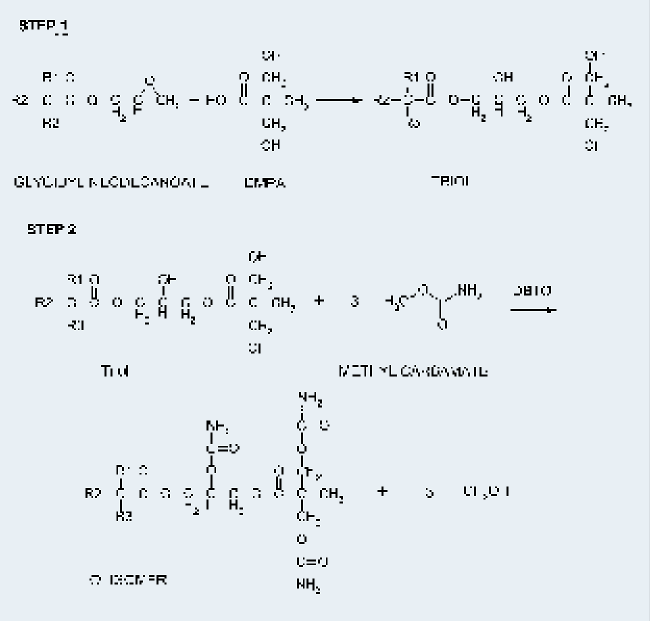


Figure 2—Oligomer synthesis.

while maintaining low VOC and acceptable environmental etch resistance. However, after years of field testing at Florida test sites and numerous field surveys, two-component urethane clearcoats are still considered by automotive manufacturers to offer the best etch resistance of all available commercial OEM clearcoats.

It was found that various carbamate functional moieties can be crosslinked with standard alkoxylated melamine to produce the desired urethane bridges via nonisocyanate avenues[15] that result in one-component clearcoats with good etch resistance and a very favorable balance of other achievable properties (*Figure* 1, bottom). The key to this technology is the resistance to acid catalyzed hydrolysis and the irreversible nature of the attractive urethane crosslinks formed and, consequently, their resistance to chemical and environmental etching along with excellent short- and long-term durability. This paper describes the synthesis and formulation of one type of these carbamate moieties that has shown low VOC, high T_g, and excellent physical properties for use in a single package automotive topcoat.

EXPERIMENTAL

Oligomer Synthesis

A series of low molecular weight oligomeric models was synthesized to determine their effect on a number of physical properties deemed necessary for a high quality automotive clearcoat.[16]

In the first step, 120 g of dimethylolpropionic acid (DMPA), a 25% aliquot of the stoichiometric ratio, was charged with 900 g of glycidyl neodecanoate to a reaction vessel (*Figure* 2). The mixture was heated to a temperature of 128°C. After a slight exotherm, three more 25% increments of 120 g of DMPA were added spaced over a four-hour period and the temperature was maintained at 130°C. The reaction was monitored via acid number to a value of < 3 and contained no residual epoxy.

In step two, 1,211 parts of methyl carbamate, a 50% excess, was added along with 10 parts of dibutyltin oxide catalyst and 950 parts of toluene. A reflux temperature of 109-117°C was maintained for 30 hr as methanol was trapped off. The progress of this reaction was monitored by hydroxyl number, to at least a 95% completion value. The excess methyl carbamate and solvent were stripped off and 450 parts of amyl acetate was added to reduce to a nonvolatile content of 80%. Gel permeation chromatography (GPC) (*Figure* 3) showed a molecular weight Mn of 751 and a polydispersity of 1.1.

Seven other hydroxy acids were used to synthesize oligomers with varying carbamate equivalent weights and varying molecular weights using this synthesis method (*Figure* 4). Two of the polyols, 2,4 dihydroxy benzoic triol and mucic hexol, could not be further processed since they were not soluble in the toluene at the reflux temperature for transesterification. In spite of their relatively low molecular weights, the other six oligomers were noncrystalline, thick liquids at 100% solids at room temperature (*Table* 1).

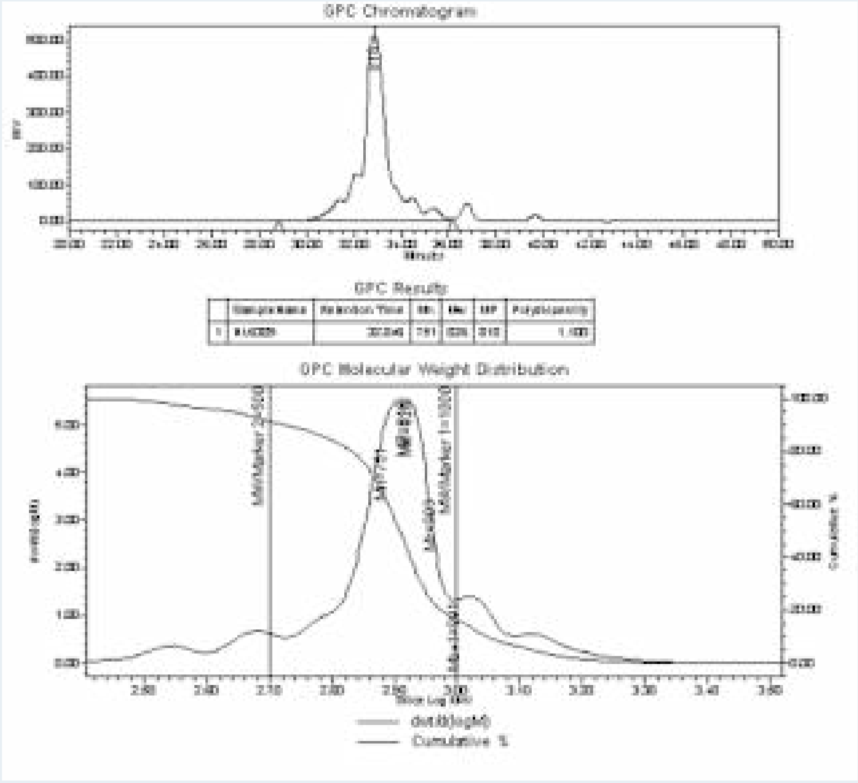


Figure 3—GPC molecular weight of carbamate oligomers.

Clearcoat Formulations

The different oligomers with varying amounts of carbamate functionality were each formulated with stoichiometric amounts, based on a 1/1 ratio of oligomer equivalent weight to melamine equivalent weight, of hexamethoxymethylmelamine (HMMM),UV absorber package, catalyst, and flow additive as indicated in *Table* 2. They were then reduced to a spray viscosity of 35 sec on a Ford #4 viscosity cup at 80°F, and the weight nonvolatiles determined according to ASTM D 2369 (1 hr @ 110°C). The experimental samples were all applied via air-atomized spray gun wet-on-wet over a conventional black high-solids solvent-based basecoat which was sprayed over 4 × 12 in. electrocoated steel panels. The basecoat film thickness was 0.7 mil (17.8 µm) and the clearcoat film builds were 1.8-2.0 mil (45.7-50.8 µm). After application the panels were allowed to flash at ambient temperature for 10 min and then baked in a gas-fired convection oven

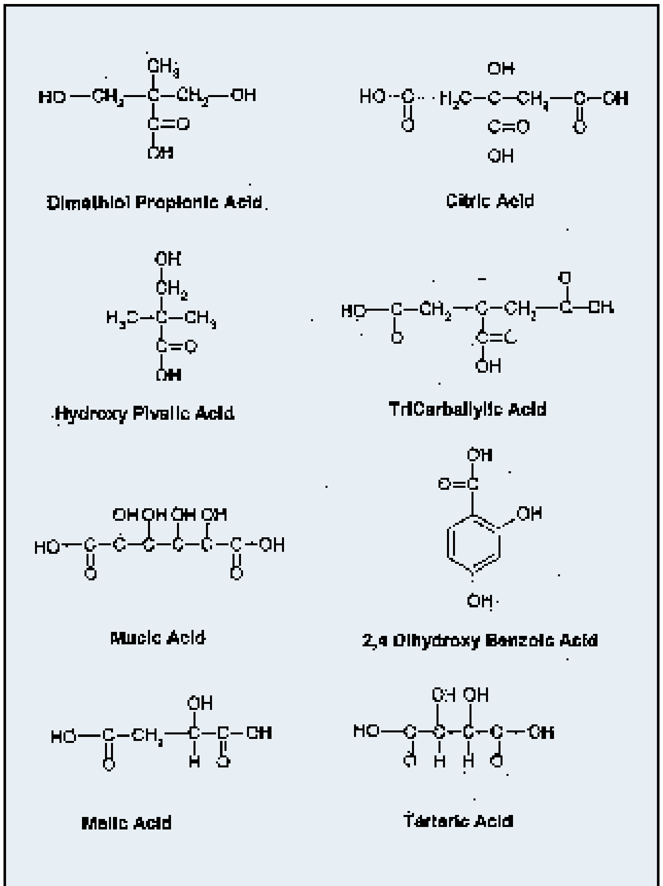


Figure 4—Hydroxy acids.

for 20 min at 265°F (129.4°C) metal temperature. Controls included in the set were three standard production samples; hydroxyl acrylic/melamine, two-component acrylic/polyurethane, and a blocked urethane/acrylic polyol clearcoat. The blocked urethane control had to be baked for 20 min at 285°F (140.5°C). Physical tests were run as follows (*Table* 3).

Physical Testing

Lab Etch Test: This accelerated laboratory test was used to predict the etch resistance of coatings when exposed to acid rain and particulate contamination in the field. Five drops of dilute electrolyte solution containing potassium chloride with traces of fumaric acid and monocalcium phosphate were individually applied to the cured film of a 4 × 12 in. steel panel. The drops were allowed to dry at room temperature for three hours. The panels were then placed on a rack in a 50°C oven for 30 min. Then one drop of 1% aqueous sulfuric acid was placed over each cluster of salt crystals on the warm panels. They were then allowed to heat for one hour in the 50°C oven. After the panels were cooled to room temperature they were washed with cool water, dried off, and evaluated for etch intensity.

The degree of etching was rated on a scale of 0-5, with 0 being no etch, and 5 being a complete failure. The two-package urethane control showed the least etching at a 1 rating; the DMPA, malic, and citric carbamate clearcoats, as well as the one-package blocked urethane clearcoat, were close behind with a 2 rating. The hydroxy pivalic, tartaric, and tricarballylic clearcoats had a 3 rating (me-

Table 1—Hydroxy Acid Polyols and Carbamates

	Hydroxy Acids	FW	MP	COOH	OH		
1	Hydroxy pivalic	118.00	125	1	1		
2	Dimethylol propionic	134.13	190	1	2		
3	2,4 Dihydroxy benzoic	154.12	226	1	2		
4	Malic	134.09	132	2	1		
5	Tartaric	150.09	173	2	2		
6	Mucic	210.14	215	2	4		
7	Tricarballylic	176.12	161	3	0		
8	Citric	192.12	157	3	1		
	Polyols	**Moles N-10**	**Moles Carb**	**WTNV**	**OH Eq Wt**	**Carb Eq Wt**	**THEO MW**
1	Hydroxy pivalic	1		100	191		381
2	Dimethylol propionic	1		100	132		397
3	2,4 Dihydroxy benzoic	1		—[a]	—		—
4	Malic	2		100	213		638
5	Tartaric	2		100	164		654
6	Mucic	2		—[a]	—		—
7	Tricarballylic	3		100	311		932
8	Citric	3		100	245		981
	Carbamate Oligomers						
1	Hydroxy pivalic	1	2	72.17		234	467
2	Dimethylol propionic	1	3	72.6		175	526
3	2,4 Dihydroxy benzoic	1	3	—[a]		—	—
4	Malic	2	3	74.73		256	767
5	Tartaric	2	4	68.33		207	826
6	Mucic	2	6	—[a]		—	—
7	Tricarballylic	3	3	76.4		354	1061
8	Citric	3	4	79.21		288	1153

(a) 3 & 6 not made; were not soluble at low enough temperature.

Table 2—Experimantal Clearcoat Formula

	Non-Volatile	Weight (g)
DMPA carbamate oligomer	67.72	79.76
Resimene 747 HMMM	26.63	26.63
Tinuvin 384 UV absorber	3.05	3.21
Tinuvin 123 HALS	1.5	1.5
Byk 306 dimethylpolysiloxane	0.1	0.8
Nacure 5225 acid catalyst	1	4
Exxate 1000 oxo-decyl acetate		7
Methyl isoAmyl ketone		33.35
	100	156.25

dium etch) and the hydroxyl acrylic clearcoat had a 5 rating (failure).

Knoop Hardness: A useful test of cure is to measure the Knoop hardness in which a pyramidal diamond stylus is pressed into the cured film to cause indentation.[17] This method is described in ASTM D 1474. In this case, a weight of 25 g was applied to the indenter for a specific time, and the length of the indentation line was measured with the microscope scale. Hardness values were taken in triplicate and the average reported. Higher numbers mean harder films and usually indicate more crosslinking and/or higher T_g.

The hardness readings ranged from 17 knoops for the DMPA carbamate clearcoat to 5.7 knoops for the tricarballylic carbamate clearcoat. All the clearcoat indentations indicated good crosslinking. Field experience has shown that at least a 6 to 8 knoop hardness is desirable to avoid undue in-service film damage.

MEK Solvent Resistance: The resistance of the cured film to solvent wiping is often used as a check for cure properties. While not always a good indicator, especially for through cure, it does give a quick read and it is a standard test for most automotive coatings. The test panels were rubbed with solvent saturated cheesecloth that has been wrapped around the head of a 16 oz ball peen hammer. One three-inch back and forward motion constitutes one double rub. Methyl ethyl ketone was used as the solvent, 200 double rubs were completed on each sample in the same area, and the cheesecloth was resoaked every 25 double rubs. The rating scale was 0-5 with 0 = best. All the clearcoats tested did well except the hydroxy pivalic carbamate system, which received a 4 rating and became softened rather easily.

Crockmeter (Scratch and Mar): A number of test methods and apparatus set-ups have been used to attempt to duplicate and test the scratch and mar resistance of automotive coatings. The Crockmeter method used in this study entailed determining the initial gloss of each 4 × 12 in. coated panel at three points. The panel was then marred at these areas using the mechanically driven Crockmeter with 3M polishing paper. The final gloss of each mar was then determined and the average gloss retention was calculated. The scratch and mar readings ranged from an outstanding 88.9% gloss retention for the DMPA carbamate clearcoat to 51.4% for the tricarballylic carbamate clearcoat. Both DMPA carbamate and the citric carbamate experimental clearcoats were equal to the hydroxyl acrylic control clearcoat and much better than the two-package urethane clearcoat for scratch and mar.

Cold Gravelometer: The 4 × 12 in. test panels were conditioned for four hours in a –20°F freezer gravelometer room prior to testing. A standard gravelometer was used to fire one pint of cold gravel at 70 psi at each panel. They were then allowed to return to room temperature, washed off, taped to remove any loose paint, and evaluated against standard charts for amount of damage. There was almost no difference between any of the panels including the controls and all were given a 4 (good) rating on a 1-10 scale (1=best), except the tricarballylic carbamate clearcoat, which was slightly worse at a 5 rating.

Humidity: Test panels were prepared for humidity testing by covering the bottom three inches of 4 × 12 coated steel panels with Wrap Guard. Some automotive plants like to cover their units with a pressure-sensitive temporary plastic film to protect the finish during shipping. This "Wrap Guard" can trap moisture underneath which results in spotty whitening of a weak basecoat/clearcoat film referred to as tracking. After application, the panels were subjected to standard humidity cabinet testing (100°F, 100% RH) for 10 days. At completion the Wrap Guard was removed, the panels patted dry, intercoat adhesion to the basecoat (ICA) checked by scribe and tape pull, and

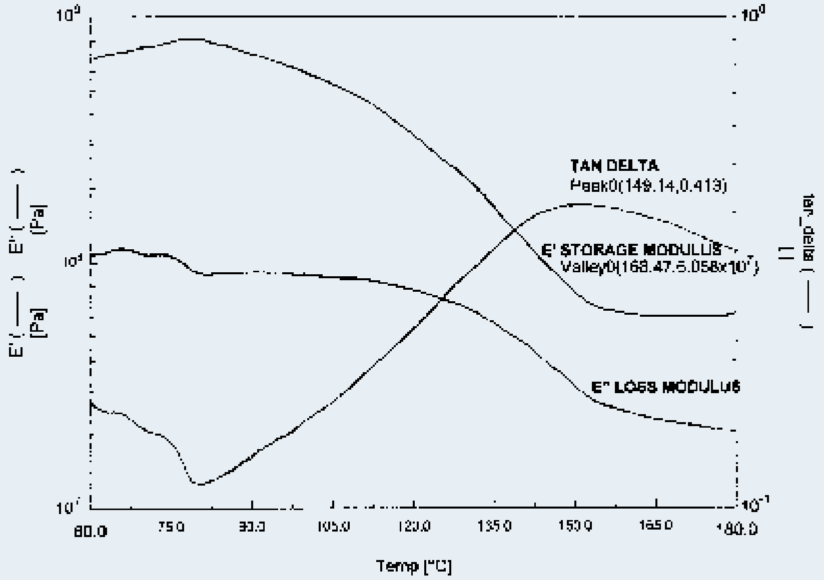
Table 3 Clearcoat Physical Properties

Vehicle	WTNV	VOC	Etch	Knoop	MEK	S&M	Gravel	Humidity	Jax-14 wk
Hydroxy pivalic	68.0	2.65	3	10.2	4	62.1	4	1,3,1,3	6
DMPA	64.0	2.99	2	17.0	1	88.9	4	1,1,1,1	3
Malic	66.5	2.75	2	10.8	2	71.7	4	1,2,1,2	4
Tartaric	64.5	2.96	3	10.9	2	73.6	4	1,1,1,1	7
Tricarballylic	67.5	2.72	3	5.7	2	51.4	5	1,1,1,2	8
Citric	66.0	2.83	2	10.0	1	82.1	4	1,1,1,1	3
Controls									
OH acrylic	56.8	3.50	5	7.8	2	85.5	4	1,1,1,2	10
2 K urethane	56.0	3.70	1	14.0	1	65.4	4	1,1,1,1	3
1 K urethane	53.3	3.80	2	8.4	1	73.2	4	1,1,3,3	5

0-5 Scale, 0= Best
Gravel and jax, 1-10 Scale, 1= Best.
Scratch and mar= % gloss retention.
Humidity= ICA, blister, blanch, tracking.

Table 4—Photooxidation Rate on Xenon Weatherometer (4000 hr) (Percent Area Change per Hour of OH, NH, and COOH Groups)

Sample	Photooxidation Rate No UVA or HALS 10^{-3} Photooxidation/hr	Photooxidation Rate With UVA & HALS 10^{-3} Photooxidation/hr
DMPA	0.25	0.18
Citric	0.51	0.16
OH acrylic	0.54	0.20
2K urethane	0.39	0.15
1K urethane	0.30	0.13



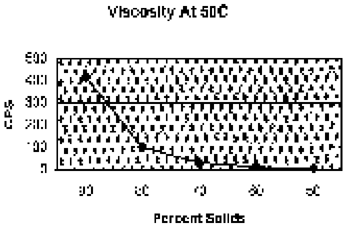
	T_g	Crosslink Density
Dimethylol propionic	**149.1°C**	**5500 mol/m^3**
Hydroxyl acrylic	**125.2°C**	**3200 mol/m^3**
2 K urethane	**139.3°C**	**860 mol/m^3**
1 K urethane	**88.3°C**	**1000 mol/m^3**

Figure 5—Dynamic mechanical analysis.

Table 5—Bohlin CS Viscometer, Temperature-Viscosity Studies

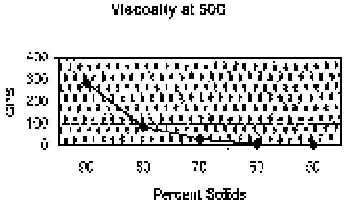
DMPA Oligomer Clearcoat

Percent Solids	Viscosity CPS 20°C	35°C	50°C
90	11742	1810	421.3
80	1263.8	307	101.2
70	238.9	79.2	32.91
60	65.5	26.91	12.99
50	19.59	10.78	5.6



Citric Oligomer Clearcoat

Percent Solids	Viscosity CPS 20°C	35°C	50°C
90	9245	1625	287
80	955	258	88
70	201.2	70.5	29.2
60	49.9	20.4	8.5
50	11.8	5.6	3.3



then they were evaluated for ICA, blistering, blanching or whitening, and amount of visible tracking.

In general, the humidity resistance was very good on all the samples tested. There was no sign of adhesion loss on the ICA tape on any of the samples. There was some slight blistering on the malic and hydroxy pivalic oligomer samples. There was no whitening on any samples except the single-package urethane, but there was some visible tracking on the hydroxy pivalic, malic, tricarballylic, hydroxyl acrylic, and single-package urethane panels.

Jacksonville Field Etch: Panels were prepared for summer exposure at the Jacksonville, FL, Blount Island site by spray application of the various clearcoats over standard black high-solids basecoats on 10 × 10 in. electrodeposition coated steel panels. These panels were then exposed in a horizontal position on racks for 14 weeks. Periodically during the summer, they were rinsed off with water and evaluated for visible etching. In the fall, at the end of the 14-week exposure period, they were given a final rinse and rated again for etch resistance. A 1-10 scale was used and comparisons were made to standard etch panels. A 1 to 3 etch rating was excellent with only slight, not readily perceived, etches. A 4 to 6 rating indicated intermediate etching which could possibly be noticed and returned for repainting by the average owner, while a 7 to 10 rating was readily apparent and would be unacceptable for any customer.

Two of the experimental systems, DMPA carbamate and citric carbamate clearcoats, were rated excellent, equal to the best two-component urethane. The hydroxy pivalic carbamate and malic carbamate clearcoats were rated mediocre, equivalent to the typical single-package blocked urethane system. Two samples, the tartaric carbamate and the tricarballylic carbamate clearcoats, were rated poor, only slightly better than the hydroxyl acrylic control. In subsequent years, the DMPA carbamate and the citric carbamate systems were exposed on full auto hoods along with production controls and were confirmed to exhibit excellent etch resistance under a variety of exposure conditions.

Exposure Durability: A number of accelerated weathering tests, as well as South Florida exterior exposure tests, were run to test the durability of the carbamate oligomer clearcoats. QUV and Xenon Arc Weatherometer tests both showed 85-90% gloss retention on the experimental carbamate systems after 4,000 hr exposure. Thirty-six-month South Florida exposures on a 5° south black box rack over a variety of basecoat colors showed an average gloss retention of 80-90%. In-house accelerated photooxidation testing was run on the different systems with and without the UV absorber package in the Xenon weatherometer. This test measured the growth of OH, NH, and COOH groups in the sample due to UV degradation, as measured by transmittance IR. Results indicated the carbamate oligomers had a similar photooxidation rate to the 1K and 2K urethane clearcoats (*Table* 4).

VOC Calculations: The weight nonvolatile values of the experimental systems were determined using ASTM 2369 and the results used to calculate the VOC according to ASTM 3960. The pounds of VOC per gallon (lb VOC/gal) of clearcoat ranged from 2.65 for the hydroxy pivalic carbamate to 2.99 for the DMPA carbamate. All of these VOCs were well below those of currently available commercial clearcoats and offered significant reductions in solvent emissions. This would, of course, allow welcome latitude in drafting complete assembly plant VOC compliant paint systems.

In addition to the listed physical testing, a number of other properties were run to characterize and compare the carbamate oligomers with other experimental systems as well as currently used commercial clearcoats. Some of these other properties tested, with very positive results, were vertical and horizontal appearance, application windows, multiple layer intercoat adhesion, acid resistance, hot-box stability, and yellowing at overbake conditions.

DMA: Dynamic mechanical analysis (DMA) was run on free film samples of clearcoats only, sprayed over mylar films. Razor cut samples (6 mm × 8 mm × 0.1mm thick) were prepared and then scanned from 60 to 180°C on a Rheometrics DMTA V instrument run at 3.1 Hz oscillating frequency. The height of the tan delta max peak was used to determine the T_g of the cured film and the E′ (minimum) value was used to calculate the crosslink density according to the formula: crosslink density $\upsilon_e = E'/3RT$. The two highest T_g clearcoats tested were the DMPA carbamate and the two-component urethane. The DMPA carbamate clearcoat had a cured film T_g of 149.1°C compared to 139.3°C for the two-component acrylic/urethane and a crosslink density of 5500 mol/m^3 compared to 860 mol/m^3 for the 2K (*Figure* 5).

Hot Spray

A Bohlin CS viscometer was used to map out the viscosities at varying temperatures and solids of the carbamate oligomer clearcoats (*Table* 5). It was found that there was definitely not a linear relationship with time and temperature at each solids level. At the lower temperature (20°C) there were substantially higher viscosities, and a large difference in viscosity between the 80% and the 90% solids samples. At higher temperatures, however, there was an abnormally large decrease in viscosity. This suggested the possibility of spraying at elevated temperatures to obtain very high-solids systems.

A larger batch of the carbamate oligomeric clearcoat was made up at 85% weight nonvolatiles (1.3 VOC) using the citric oligomer processed at 100% solids. This clearcoat was put in a minicirculation system, heated to 50°C (122°F), and hot sprayed wet-on-wet over a standard black, high-solids basecoat. The appearance was good but required that all the clearcoat solvent in the system be replaced with a slow tail solvent and that the rheology control package be lowered. Also, the minibell inlet connections had to be shortened to keep the material hot right to the gun. Most assembly plants are already equipped with heat exchangers on the feed lines to control the incoming paint temperature, so spraying at an elevated temperature was not an expensive concept.

CONCLUSIONS

Representing a new class of resins, carbamate functional moieties were shown to give the desirable qualities of a urethane crosslink with the convenience and economics of a one-package system. The carbamate functional oligomers described in this paper have been shown to possess the good balance of physical properties necessary for an automotive OEM topcoat system. A bonus was the improvement of solids and VOC, from the current average in automotive assembly plants of 55% weight nonvolatile and a VOC of 3.8 lb/gal to an attainable 64% weight nonvolatiles and a VOC of 2.99 lb/gal, and a possible 85% weight nonvolatile and a VOC of 1.3 lb/gal using hot spray techniques. The Jacksonville environmental etch studies on these systems have shown them to be equal to two-component urethane clearcoats. The laboratory scratch and mar tests showed the carbamate oligomers to be much superior to the two-component urethanes. The humidity resistance, accelerated weathering, as well as South Florida exposure all indicated these carbamate clearcoats have excellent UV durability and hydrolysis resistance.

ACKNOWLEDGMENTS

I would like to especially recognize the contributions and help given by other members of the BASF Clearcoat Development team: J.E. Boisseau, B.E. Oermann, D.L. St. Aubin, W.H. Ohrbom, D.H. Campbell, H. Turner, J.W. Rehfuss, and P.K. Oberg (Analytical).

References

(1) Private Communication, Martin, G.E. and Wolff, G.T., "Environmental Etching of Automotive Coatings, Joint Research Study," BASF internal research report, Poly 264-92 (1990).

(2) Wolff, G.T. and Rogers, W.R. et. al, "Spotting of Automotive Finishes from the Interactions Between Dry Deposition of Crustal Material and Wet Deposition of Sulfate," *J. Air Waste Manage. Assoc.*, 40, 1638 (1990).

(3) Armstrong, V.C., Farlow, D.W., and Moodie, R.B., "The Hydrolysis of Amides, Esters, and Related Compounds in Acid Solution. Part I. Amides, Carbamates, and Ureas," *J. Chem. Soc. B*, 275 (1968).

(4) Armstrong, V.C. and Moodie, R.B., "The Hydrolysis of Amides, Esters, and Related Compounds in Acid Solution. Part II. Carbamates," *J. Chem. Soc. B*, 937 (1969).

(5) Payne, K.L., Jones, F.N., and Brandenburger, L.W., "Hydrolytic Stability of Oligoesters in Simulated Water-Reducible

Coating Formulations," JOURNAL OF COATINGS TECHNOLOGY, *57*, No. 723, 35 (1985).

(6) Peijnenburg, W.J.G.M., "The Use of Quantitative Structure-Activity Relationships for Predicting Rates of Environmental Hydrolysis Processes," National Institute of Public Health and Environmental Protection, Laboratory of Ecotoxicology, Bilthoven, The Netherlands, IUPAC, 1991.

(7) Pourdeyhimi, B., Wang, X., and Lee, F., "Evaluation of Scratch and Mar Resistance in Automotive Coatings," *Eur. Coat. J.*, 3, 75, 1999.

(8) Gregorovich, B.V. and Hazan, L., "Environmental Etch Performance, Scratch and Mar of Automotive Clearcoats," *Prog. Org. Coat.*, 24, 131, 1994.

(9) Chen, M.J., "Moisture-Curable Silylated Acrylic Clear Coats—Improvements in Mar Resistance," Presented to Detroit Society for Coatings Technology, OSI Specialties Inc., December 1995.

(10) Ryntz, R.A., Abell, B.D., Pollano, G.M., Nguyen, L.H., and Shen, W.C., "Scratch Resistance Behavior of Model Coating Systems," JOURNAL COATINGS TECHNOLOGY, *72*, No. 904, 47 (2000).

(11) Hill, L.W., "Mechanical Property/Property Relationships in Coatings," *ACS, PMSE Preprints*, American Chemical Society, Washington, D.C., 79, 405, 1998.

(12) Gregorovich, B.V. and McGonigal, P.J., "Mechanical Properties of Coatings Needed for Good Scratch and Mar," in *Proc. Advanced Coatings Technology Conference* ASM/ESD, 1992.

(13) Courter, J.L., "Mar Resistance of Automotive Clearcoats: 1. Relationship to Coating Mechanical Properties," JOURNAL OF COATINGS TECHNOLOGY, *69*, No. 866, 57 (1997).

(14) Gregorovich, B.V. and Hazan, L., "Environmental Etch Performance and Scratch and Mar of Automotive Clearcoats," *Proc. XIXth International Conference in Organic Coatings Science and Technology*, 19, 205-218, Athens, Greece, 1993.

(15) Rehfuss, J.W. and St. Aubin, D.L., "Composite Color-Plus-Clearcoating Utilizing Carbamate-Functional Polymer Composition in the Clearcoat," U.S. Patent 5,356,669, October 18, 1994.

(16) Green, M.L., "Low VOC Curable Coating Compositions Utilizing Carbamate-Functional Compound," U.S. Patent 5,693,724, December 2, 1997.

(17) Koleske, J.V., "Physical and Mechanical Properties: Hardness," *Paint and Coatings Testing Manual*, Gardner-Sward Handbook, ASTM: MNL 17, Philadelphia, PA, 1995.