Cure of Secondary Carbamate Groups by Melamine-Formaldehyde Resins

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Melamine-formaldehyde (MF) resins have been used as crosslinkers for hydroxyl-functional co-reactants in thermoset coatings for about 60 years. Crosslink densities of films prepared from oligomeric urethane polyols suggested that the methoxymethyl groups of MF resins could react with urethane groups (i.e., secondary carbamate groups) as well as reacting with hydroxyl groups. Co-reactants that contain secondary carbamate groups and no hydroxyl groups have been prepared with several types of backbone structures. Cure of such co-reactants by MF resins has been studied using a gradient oven with determination of impact resistance, solvent resistance, and hardness. Several formulations from these cure profile sets have been selected for crosslink density determinations by dynamic mechanical analysis (DMA). Crosslink densities of cured films are consistent with complete conversion of secondary carbamate groups at temperatures only slightly higher than those used for cure of hydroxyl groups. The –OH groups on certain acrylic polyols were converted to secondary carbamate groups. The original acrylic and the converted acrylic were both cured with MF resins. Acid resistance was much better for films prepared from the acrylic that contained secondary carbamate groups.

INTRODUCTION

Amino resins are reported to be the predominant crosslinking agents for thermosetting industrial coatings, and melamine-formaldehyde (MF) resins are the most widely used type of amino resin.[1] MF resins have been used extensively to crosslink hydroxyl-functional acrylic or polyester co-reactants for over 60 years.[2] Other groups that are known to react with MF resins include carboxylic acids, amines, and amides.[2] Recently Blank[3] stated that secondary carbamate groups in urethanes are potentially reactive with MF resins but that no publications have specifically discussed this subject. The purposes of the work reported here are to demonstrate unequivocally that MF resins do react with secondary carbamate groups and to investigate possible advantages of using this reaction in commercial thermoset curing.

Gregorovich and Hazan[4] reported that the use of polyol/melamine binders in automotive clearcoats gives excellent appearance and low VOC, but that environmental pollutants and especially acid rain, cause permanent spotting and pitting known as "environmental etch." Gardon[5] and Walker et al.[6] synthesized novel polyurethane polyol oligomers by reacting aliphatic di-functional or tri-functional isocyanate monomers with diols. Surprisingly, 1, 2- and 1,3-diols were observed to react primarily single-endedly which favored oligomers of narrow molecular weight distribution. Yahkind et al.[7] prepared similar oligomers but viscosity was reduced by inclusion of some mono-functional alcohol along with the diols. When the polyurethane oligomers were crosslinked with MF resins, the resulting films were reported to have improved acid rain resistance, weatherability, and scratch resistance relative to MF-cured acrylic polyol films. Results of current work suggest that urethane groups on these oligomers react with MF groups to improve acid resistance.

MF resins have been used to crosslink acrylic resins which contain primary carbamate groups [–O(C=O) NH_2] in place of the more common –OH groups, and these primary carbamate/MF systems give automotive clearcoats with improved etch resistance.[8,9] The secondary carbamates studied here provide a less polar alternative to the primary carbamate systems.

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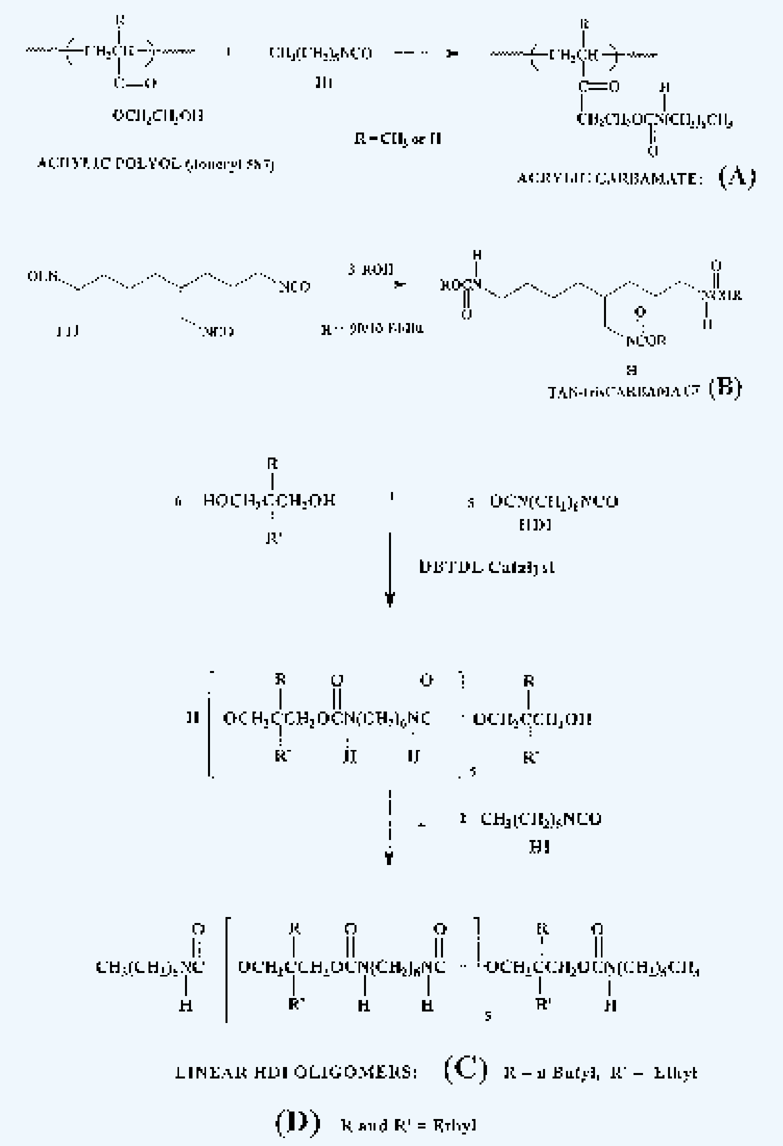

Figure 1—Synthesis of secondary carbamate Co-reactants A-D.

EXPERIMENTAL

Materials

2-Butyl-2-ethyl-1,3-propanediol (BEPD), 2,2-diethyl-1,3-propanediol (DEPD), and n-hexyl isocyanate (HI) were obtained from Acros Organics. Phenyl isocyanate (PI), butyl isocyanate, tolylene 2,4-diisocyanate (tech 80%) (TDI), dibutyltin dilaurate (DBTDL), and 2-ethylhexanol were all obtained from Aldrich. 1,6-hexamethylene diisocyanate (Desmodur® H) (HDI) and HDI-Trimer (Desmodur® N-3300) (HDI-Tri) were obtained from Bayer. TAN-triisocyanate (TTI) was prepared by methods previously reported.[10] Joncryl® 587 hydroxyl functional acrylic was obtained from S.C. Johnson. Each of the materials was used as supplied.

MF Resin I is a laboratory model synthesized to be highly monomeric and highly alkoxylated, approximating the structure of hexamethoxymethyl melamine (HMMM). The other MF resins used in this work are commercial products* that were selected to give a wide range of alkoxylation and degree of polymerization as indicated in *Table* 2.

Synthesis

Model polyfunctional carbamate co-reactants were synthesized with careful control of stoichiometric imbalance of isocyanates and polyols to obtain desired molecular weights and end-group functionalities. A monofunctional model carbamate was prepared by reaction of 2-(ethyl)hexanol with butyl isocyanate. Reactions were run in a rotary evaporator set-up with a temperature controllable water bath. Reactions were run under dry nitrogen using dry, alcohol-free chloroform as a reaction solvent. Generally, 0.01 phr of DBTDL catalyst was added. Reactions were held at 25°C for two hours and were then heated to 70°C and held until completeness of reaction could be confirmed by FTIR. The completed reaction was stripped of volatiles under vacuum by heating at 70°C. When end capping a polyol intermediate with a mono-isocyanate, it was often desirable to add excess of the mono-isocyanate to insure complete reaction of all residual hydroxyls. The excess isocyanate could be reacted with dry ethanol to form a monocar-bamate. The monocarbamate and any alcohol could then be vacuum stripped from the product. When branched diols were used, the oligomeric urethanes prepared in this manner were soluble in ketone solvents and could be readily formulated with MF resins in solution form.

Methods

The secondary carbamate models A-E in solution (see *Table* 2) were readily formulated with MF resins, unblocked pTSA catalyst (0.5 parts per 100 parts binder solids), and acrylic flow and leveling agent (Modaflow® resin from Solutia Inc.) (0.5 part per 100 parts binder solids). These formulations displayed excellent storage stability which was better than typically observed with MF resins formulated with polyol co-reactants in the presence of unblocked acid catalysts. Only the aromatic model, Carbamate F, had to be warmed slightly prior to application in order to fluidize the associative gel which formed on standing. Formulation viscosities were low enough for drawdown application at 60 to 70% solids. A drawdown bar with a 7 mil (175 μ) gap resulted in cured films having 1.2 to 1.4 mil (30 to 35 μ) dry thickness. The substrates used for cure profile

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*MF resins designated II, III, IV, V and VI are Resimene® crosslinkers R-747, R-755, R-717, HM-2608 and AQ-7550, respectively, from Solutia Inc.

determinations were ACT cold-rolled steel test panels (4 in. × 22.5 in. × 0.032in. - B1000, P60, DIW, polished), and the substrates used for dynamic mechanical analysis (DMA) were 4 in. × 6 in. tin plated steel panels from Q-Panel Company. Films were glossy and had excellent appearance.

Cure profiles were determined using a gradient oven (BYK Chemie) programmed to give four cure temperature zones with adjacent zones differing by 10°C. Several temperature ranges were used with each formulation to provide cure data from 45° to 150°C. The width of the zones (about four inches) was sufficient to permit determination of impact resistance (ASTM D 2794, *Figure* 2b), Tukon hardness (ASTM D 1474, *Figure* 2c), and methyl ethyl ketone (MEK) double rub resistance (*Figure* 2a). The procedure for MEK rub resistance was a modification of ASTM D 4752 in which a hollow-barrel felt tip marker was filled with MEK. The marker was rubbed back and forth with firm pressure at a rate that gave one back and forth stroke (double rub) in about one second. This cure profile method is described in detail elsewhere.[11]

Acid resistance was tested by placing 45 droplets of 10% sulfuric acid on a film cured on a gradient oven panel (4 in. × 22.5 in. × 0.032 in.). Cure was carried out in a forced air oven at constant temperature, and the temperature gradient was used only to enhance the attack by acid. The coated panel with acid droplets was heated for 30 min in the gradient oven with temperature variations from 35° to 75°C. After 30 min, the acid droplets were rinsed off and the panel was wiped dry. The panel was inspected carefully at various angles to prevailing light to determine the lowest temperature at which damage from acid could be seen. This temperature was called "minimum spot temperature" (MST). At MST and at all spots above MST, the severity of attack was rated (scale of 0 to 5). A rating of zero corresponds to no effect, 1 corresponds to a barely observable partial ring, and 5 indicates removal of the coating down to bare metal. The sum of the ratings was manipulated [scaled value = 1.0 – (sum/225)] to give a scale from zero to 1.0. Since 5 × 45 = 225, zero means complete removal of the film to substrate by all 45 droplets, and 1.0 means no effect by any of the 45 droplets.

Dynamic mechanical analysis (DMA) was carried out on free film samples at 11 Hz oscillating frequency on an Autovibron® instrument (Imass Inc.). Tensile storage modulus (E'), tensile loss modulus (E"), and the loss tangent (tan = E"/E') were determined from 10° to 190°C at a temperature scan rate of 2°C/min. Films were removed from tin-plated substrates by mercury amalgamation, and 0.4 cm × 2.5 cm samples were die cut with a razor blade device.[12] The dynamic deformation was maintained at a small fraction of sample length (0.02%) to avoid per-

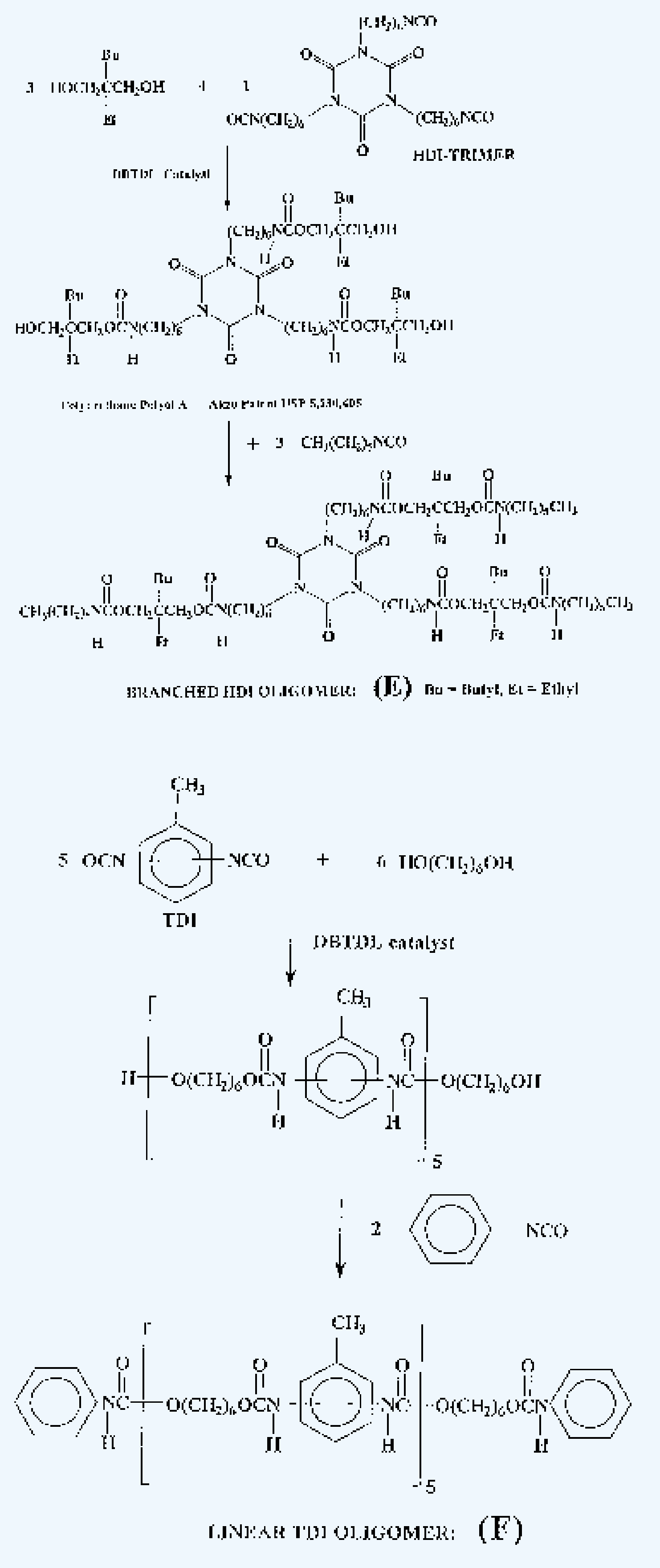


Figure 1 (cont'd)—Synthesis of secondary carbamate Co-reactants E and F.

Table 1—Model Secondary Carbamate Co-reactants

Code	Description	Components[a] (Theory Eq. Wt.)	Solution Solids %[b] (Solvent) {Vis. cps.}	Mn (GPC)	Mn/Mw (GPC)
A	Acrylic Carbamate	Joncryl 587 Polyol + HI (737)	47.5% (BuOAc) {4,500}	—	—
B	TAN-tris Carbamate	TI + 90/10 EtOH/BuOH (133)	100% (none) {65,000}	399	1.0
C	Linear HDI Oligomer	6 BEPD + 5 HDI + 2HI (172)	75.3% (MEK) {5,500}	1,996	1.6
D	Linear HDI Oligomer	6 DEPD + 5 HDI + 2HI (157)	72.6% (MEK) {4,200}	2.094	1.7
E	Branched HDI Oligomer	1 HDI-Tri + 3 BEPD + 3 HI (235)	62.5% (MIAK) {2,100}	1,609	3.7
F	Linear TDI Oligomer	6 HD + 5 TDI + 2 PI (152)	62.0% (MEK) {Gels cool}	2,221	2.2

(a) TTI = Tan-triisocyanate, HI = n-hexylisocyanate, DEPD = 2,2-diethyl-1,3-propanediol, HDI = hexamethylene diisocyanate, BEPD = 2-butyl-2-ethyl-1,3-propanediol, HDI-Tri = HDI Isocyanurate trimer of HDI (Desmodur N-3300), HD = 1,6-hexemethylenediol, TDI = toluene diisocyanate, PI = phenyl isocyanate.

(b) BuOAc = butyl acetate, MEK = methylethyl ketone, MIAK = methyl isoamyl ketone. Viscosities measured on a Brookfield CAP Visc. @ 25°C, 100 rpm.

manent deformation or breakage. This facilitated carrying the scan through the full range of polymer behavior from glassy through transition behavior and finally well into the rubbery plateau at high temperatures. Properties that were used to determine the extent of cure included the minimum value of storage modulus in the rubbery plateau, E′(min); the height of the tan peak for the glass transition, tan δ (max); and the glass transition temperature, T_g, taken as the scan temperature at tan δ (max).[12] The width of the tan peak measured at half height (i.e., at [tan δ (max)]/2) and expressed in °C is designated as PW (peak width). PW is useful for assessing the network uniformity,[12] and in this work PW indicates the extent of self-condensation of MF resin.

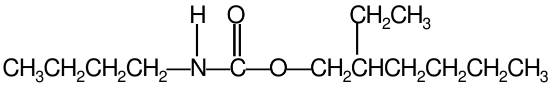
RESULTS AND DISCUSSION

Synthesis and Characterization of Secondary Carbamate Co-reactants

Oligomeric urethane polyols are frequently crosslinked with MF resins,[5-7] but papers usually do not discuss the nature of the crosslinking reaction. The implication is that crosslinking occurs through hydroxyl groups just as it does with polyester or acrylic polyols. The co-reactants prepared for this work were designed to have no –OH groups at all as shown in *Figure* 1. Observation of cure with such co-reactants strongly suggests involvement of secondary carbamates in the curing reaction. Characteristics of the oligomeric secondary carbamate co-reactants are given in *Table* 1.

Two simple ways to prepare secondary carbamate co-reactants are to react a polyol with a mono-functional isocyanate or to react a polyfunctional isocyanate with a mono-functional alcohol. The –OH groups on a commercial acrylic polyol (Joncryl® 587, S.C. Johnson) were reacted with hexylisocyanate (*Figure* 1, Co-reactant A). The three isocyanate groups of triamino-nonane-triisocyanate (TTI) were reacted with mono-functional alcohols (*Figure* 1, Co-reactant B). When a 90/10 mixture of ethanol/butanol was used, the resulting mixed carbamate was a liquid with little tendency to crystallize.

A mono-functional model compound, butyl-(2 ethylhexyl) carbamate (1), was



$$CH_3CH_2CH_2CH_2{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2\overset{CH_2CH_3}{\overset{|}{C}}HCH_2CH_2CH_2CH_3 \qquad (1)$$

synthesized by reaction of butyl isocyanate and 2-ethylhexanol. Reactions of model carbamates like structure (1) with MF Resin I were followed by FTIR, ^{13}C NMR, and ^1H NMR. As described in detail elsewhere,[13] these methods confirm that N–H sites of (1) and methoxymethyl groups of MF Resin I undergo reaction with each other. The disappearance of the FTIR N–H band between 3500-3200 cm^{-1} (with some –OH back-

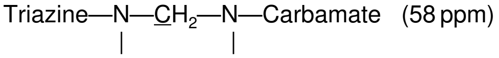
Table 2—Model Melamine Resin Crosslinkers

Code	Description[a] (Comb. Ratio) {DP} ((MW))[b]
I	Highly monomeric HMMM resin lab synthesized non-commercial model resin
II	HMMM type—high F/M—high etherification (1/5.7/5.0/0) {1.4} ((511))
III	Mixed Bu/Me co-ether type—high F/M—high etherification (1/5.7/2.8/2,2) {1.4} ((637))
IV	Me-ether type—intermediate F/M—intermediate Imino/M (1/3.7/3.6/0) {1.6} ((432))
V	Me-ether type—low F/M—high Imino/M (1/4.5/3.8/0) {1.4} ((380))
VI	Me-ether type—low F/M—high Imino/M—aqueous resin (1/2.4/1.5/0) {1.8} ((396))

(a) HMMM = hexamethoxymethylol melamine, M = melamine or triazine ring, Bu = butyl, Me = methyl, F/M = combined formaldehyde per triazine ring, Imino/M = N-H groups per triazine ring.

(b) (Combining Ratio) = melamine/formaldehyde/methyl alchol/butyl alcohol; {DP} = degree of polymerization; ((MW)) = number ave. molecular wt.

ground present) correlated distinctly with the disappearance of the methoxymethyl ether band at 916 cm^{-1} from MF. The ^{13}C NMR chemical shift (initially 67 ppm) and the ^{1}H NMR chemical shift (initially 3.95 ppm) of the methylene group attached to the oxygen of the carbamate group in structure (1), both changed slightly as the reaction proceeded. The position of the ^{13}C NMR peak assigned to the methylene carbon attached to the N atom of the carbamate group [see structure (1)] was observed to undergo greater change during reaction, from 42 to 47 ppm. A larger change is expected for this carbon atom because it is closer to the proposed reaction site. A new ^{13}C resonance grew in at 58 ppm. It was assigned to the carbon atom of a methylene group lying between two N atoms in the reaction product.



$$\text{Triazine}—\underset{|}{\text{N}}—\underline{\text{C}}\text{H}_2—\underset{|}{\text{N}}—\text{Carbamate}\quad(58\,\text{ppm})$$

This product part structure is more completely shown in *Figure* 6. Other changes in ^{13}C and ^{1}H NMR spectra were also consistent with the predominant reaction of methoxymethyl groups with carbamate N–H although the exact chemical shifts varied slightly with carbamate structure.[13]

Analytical results with solutions of mono-functional model compounds, such as (1), and peak width results from DMA (see the following) both suggest that self-condensation is not extensive under the cure conditions used here.

Two carbamate co-reactants were prepared from hexamethylenediisocyanate (HDI) reacted with selected propanediols (*Figure* 1, Co-reactants C and D). The stoichiometric imbalance was calculated to produce hydroxyl terminated oligomeric intermediates having number average molecular weights of approximately 2000 g/mole. These intermediates were then reacted with hexylisocyanate to convert the terminal –OH groups to secondary carbamate groups. Residual hydroxyl level was very low. If the propanediol selected for use had R = H or R = methyl (see *Figure* 1), the products formed associative gels which were difficult to formulate with melamine. However, if the R groups were ethyl, butyl, or mixtures of these, then the oligomeric products did not form gels. The butyl/ethyl types could be dissolved in a variety of ketone solvents and easily formulated with melamine resins. The longer alkyl side chains on the diol apparently break up hydrogen bonding.

Other secondary carbamate co-reactants were prepared to investigate structure/property relationships. For example, the synthesis of a novel polyurethane polyol, described by Gardon[5] and Walker,[6] was repeated here. In our work the terminal –OH groups were capped with hexylisocyanate to give a hydroxyl-free branched oligomer (*Figure* 1, Co-reactant E). A model oligomer with secondary carbamate groups attached to aromatic rings was prepared by reacting toluene diisocyanate (TDI) with hexane diol and capping with phenyl isocyanate (*Figure* 1, Co-reactant F).

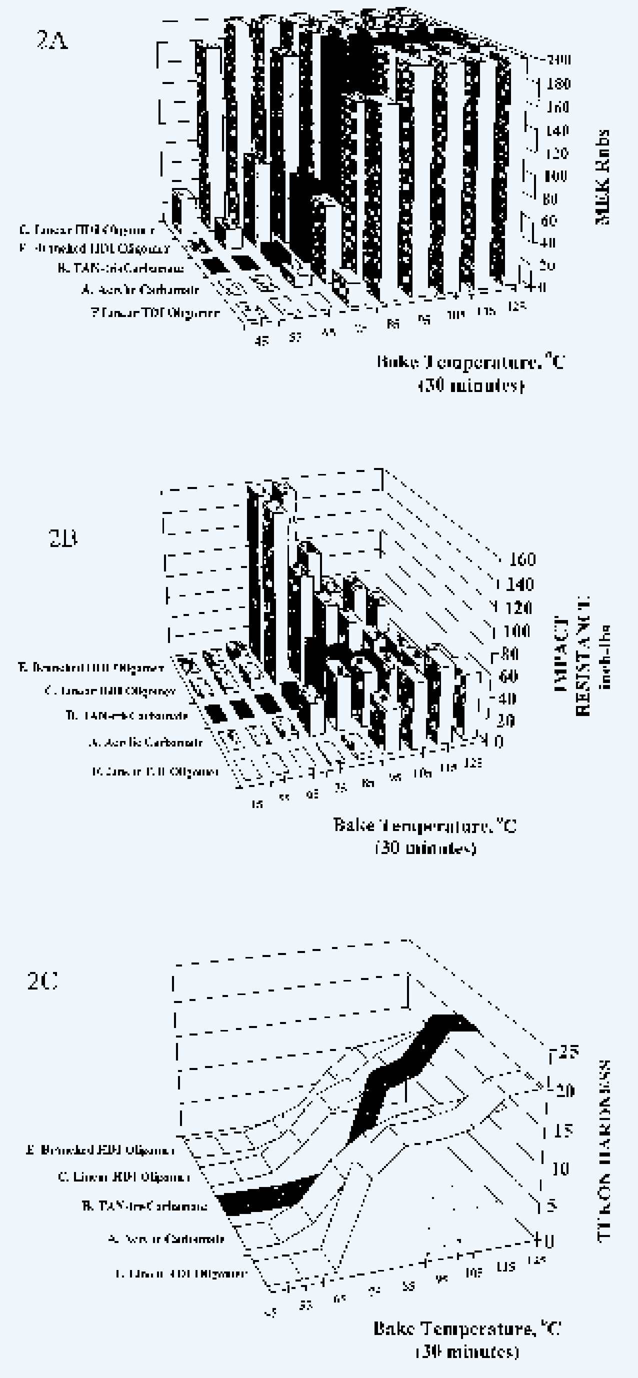


Figure 2—Cure profiles of carbamate co-reactants with monomeric MF Resin (I): (A) methylethylketone double rubs; (B) impact resistance; and (C) Tukon hardness.

As shown in *Table* 1, the various model secondary carbamate co-reactants used in this study had a rather wide range of backbone type, molecular weight, equivalent weight, and polydispersity. These characteristics are known to influence viscosity. Solution viscosities of the model carbamates in various solvents at several solids levels are reported in *Table* 1. Models A through E all formed stable solutions at the indicated solids levels without any tendency to form associative gels on storage. Carbamate A derived from the relatively high molecular weight acrylic polyol had to be diluted the most to control viscosity. However, the solution viscosity of

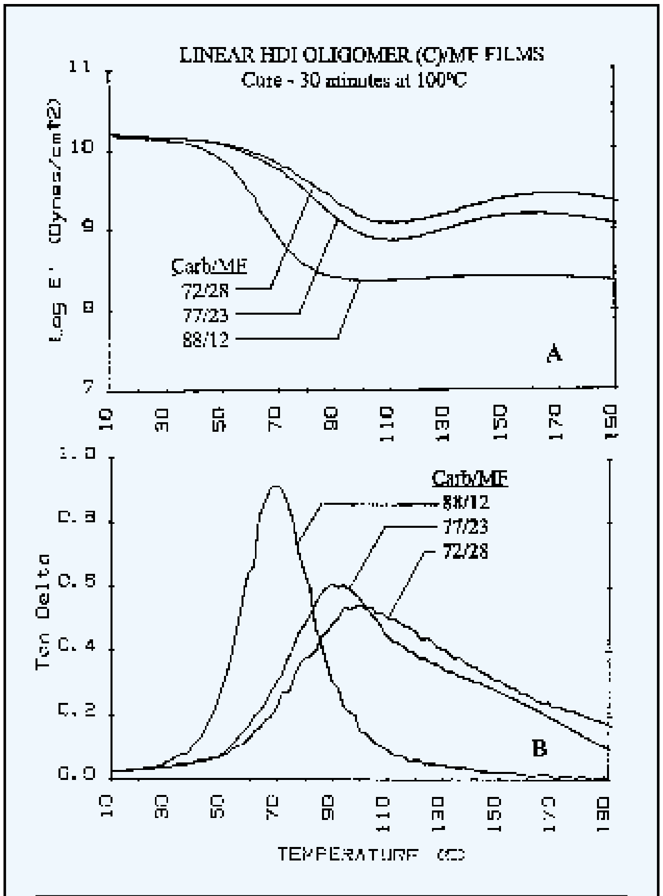


Figure 3—Dynamic mechanical analysis with Co-reactant C: (A) storage modulus, E'; (B) loss tangent, tan δ.

Carbamate A was significantly lower than that of the acrylic polyol from which it was derived. The monodisperse, low molecular weight adduct, Tricarbamate B, is a viscous liquid without dilution as shown in *Table* 2, and viscosity dropped sharply with addition of ketone solvents. Use of ethyl or butyl branched diols in synthesis of oligomeric models C, D, and E prevented formation of associative gels whereas oligomers prepared with neopentylglycol were not useful because the resulting oligomer was an insoluble gel. The aromatic model, Carbamate F, was fluid in solution when first made, but separated after storage; it could be re-fluidized by warming. It is well recognized that polyurethane polymers and oligomers are often extremely high in viscosity, and various approaches[5-7] to structure control have been used to reduce viscosity and to minimize the VOC of formulated coatings.

Cure Response of Model Carbamates in a Gradient Oven Test

Paint test results on films prepared from five of the model carbamates in *Table* 1 are shown in *Figure* 2 and *Table* 3. Co-reactant D (Linear HDI oligomer with DEPD) gave results very similar to those of Co-reactant C (Linear HDI oligomer with BEPD), and D was dropped for brevity. The MF resin used throughout this series was I, a developmental crosslinker containing high levels of HMMM as described in *Table* 2. The co-reactant/MF equivalent ratio was 1/1 in all cases. An equivalent weight of 67 g/eq was used for MF resin I whereas the theoretical value for pure HMMM is 65 g/eq. The cure catalyst was p-toluene sulfonic acid (pTSA) at 0.5 phr on binder solids, and the cure time was 30 min. The cure onset temperature for all of the model co-reactants (selected as the bake temperature where the MEK double rub value reaches 150) is 85°C or below. MEK resistance values are indicated graphically in *Figure* 2a, and at 10°C cure temperature intervals from 65° to 125°C in *Table* 3. Results in *Table* 3 indicate that among the five co-reactants, cure onset temperature increases in the order C< E<B<A<F. These reactivity differences are also evident in *Figure* 2a.

Paint film properties of impact resistance and Tukon hardness are also shown in *Figure* 2 and *Table* 3. Knoop hardness numbers in the 10 to 20 range, and the observation of maxima in the impact resistance versus cure temperature data suggest rather complete cure within the 65° to 125°C range. For most of the co-reactants (A, B, C, and E) it is evident that a significant level of cure is achieved even at the relatively low bake temperature of 100°C. Since these co-reactants do not contain any –OH groups, the observed cure is attributed mainly to reaction of secondary carbamate groups with methoxymethyl groups of the HMMM crosslinker. There may be some contribution to cure from self-condensation of the MF resin, but this contribution is believed to be minor based on the mono-functional model compound results[13] discussed previously and the peak width (PW) results discussed in the following.

As shown in *Figure* 1, model Co-reactants C, D, E, and F contain both terminal and mid-chain secondary carbamate groups. Steric considerations suggest that mid-chain groups may be too hindered to react to completion. Nevertheless, the equivalent weight values given in *Table* 1 are calculated with inclusion of both terminal and mid-chain groups. In general, the average number of functional groups per molecule is obtained as (M_n/eq

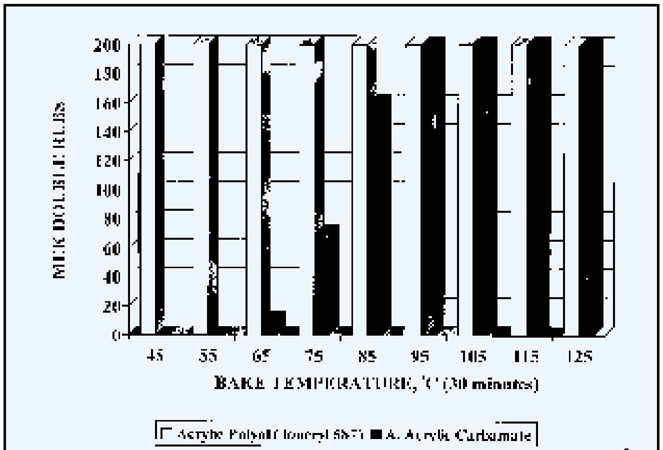


Figure 4—Cure profile data for an acrylic polyol and the acrylic carbamate (A) prepared from it. Carbamate A/MF (I) 1/1 by equivalents; catalyst 0.5 phr pTSA.

wt). For the linear HDI oligomer C, the number of functional groups per molecule is 1996/172 = 11.6, and due to the linear structure, only two of these are terminal. If none of the remaining 9.6 mid-chain carbamate groups reacted, a rather low extent of cure would be expected. Results of *Figure* 2 and *Table* 3, however, indicate a high extent of cure. We conclude that at least some of the mid-chain secondary carbamate groups, or in other words, urethane groups undergo reaction under the conditions used here. Of course, self-condensation may also contribute to extent of cure, but this contribution is believed to be minor.

Reaction of mid-chain carbamate groups with methoxymethyl groups suggests new uses for melamine resins. For example, it may be very cost effective to optimize polymer properties by crosslinking linear urethanes with melamine resins rather than using poly-functional isocyanates or polyols to obtain crosslinked urethane networks.

Results of *Figure* 2 and *Table* 3 are useful for establishing structure/reactivity relationships. As noted earlier, the lowest temperature curing secondary carbamate is the linear HDI Oligomer C followed by the branched HDI Oligomer E. Both of these have high carbamate functionality per molecule. The aromatic secondary Carbamate F is marginally slower curing than the aliphatic carbamates. The structure of Tricarbamate B differs from the other models because it is a monodisperse adduct. Its molecular weight of 399 (3 × 133) is much lower than that of the oligomeric co-reactants. The need for extensive molecular weight build-up shows up most clearly in terms of Tukon hardness (see *Figure* 2c and *Table* 3). The low hardness at the lower bake temperatures is attributed to this molecular weight effect. It is interesting to note, however, that Co-reactant B gives the highest Tukon hardness at high cure temperatures. This is attributed to its low equivalent weight which is consistent with a very tightly crosslinked network at complete conversion. The large drop in impact resistance for Co-reactant B in going from 85°C cure to 125°C cure (50 in.-lb down to 10 in.-lb, see *Table* 3 and *Figure* 2b) is also consistent with a very tight network as expected from low equivalent weight. The impact results for the linear and branched HDI models (C and E) are consistent with high functionality per molecule. Impact resistances go through a high peak (>160 in.-lb) at rather low cure temperatures and then fall to 20-40 in.-lb as crosslink density becomes higher with increasing bake temperature.

Table 3—Cure Profiles of Carbamate Co-reactants. Cured 30 min at the Indicated Temperature with Monomeric MF Resin (1)

Carbamate Id.	Cure Temp. °C	MEK Resis. Double Rubs	Tukon Hardness KHN*	Impact Resis. In.-Lb
A, Acrylic Carbamate 92/8* *Carb/MF Ratio By Weight	65	10	2	5
	75	70	7	30
	85	200	10	50
	95	200	12	50
	105	200	12	50
	115	200	13	50
	125	200	13	50
B, TAN-tris Carbamate 67/23	65	10	0	2
	75	75	0.5	30
	85	200	1	50
	95	200	14	40
	105	200	16	30
	115	200	21	30
	125	200	20	10
C, Linear HDI Oligomer (With BEPD) 72/28	65	200	1	10
	75	200	4	160
	85	200	8	100
	95	200	10	70
	105	200	13	50
	115	200	15	30
	125	200	16	20
E, Branched HDI Oligomer 78/22	65	80	0	10
	75	180	1	160
	85	200	3	160
	95	200	8	100
	105	200	11	60
	115	200	11	60
	125	200	12	40
F, Linear TDI Oligomer 69/31	65	1	0	1
	75	20	12	2
	85	170	15	5
	95	200	15	40
	105	200	16	60
	115	200	19	70
	125	200	20	60

*Knoop Hardness Number

Dynamic Mechanical Analysis of Films from Selected Co-reactants

The linear HDI Oligomer C and the branched HDI Oligomer E were selected for further cure study by DMA. The monomeric MF resin (I in *Table* 2) was used once again, and cure was carried out in a forced air oven for 30 min. DMA plots for films from the linear HDI oligomer cured at 100°C are shown in *Figure* 3. The storage modulus, E′, at the left in *Figure* 3a is characteristic of glassy polymers. The drop in E′ in the 60° to 100°C range is attributed to the glass transition, and the level of E′ at the right in the rubbery plateau region is an indication of crosslink density (XLD).[12] The film with a 72/28 co-reactant C/MF weight ratio has a very high E′(min), and as the temperature scan continues beyond the minimum, the E′ plot rises rather sharply. This rise is attributed to additional curing during the DMA scan. We conclude that 30 min at 100°C with 0.5 phr of p-toluene sulfonic acid is not sufficient to convert all of the functional groups. The unconverted groups are most likely mid-

Table 4—MF Cure of Carbamate Functional Derivatives of HDI; Cure—30 min, 0.5 phr pTSA

Cure Temp. °C	Carb/MF Wt.(Equiv.)	T_g °C	Tan δ (max)	10^{-8} x E' (min) Dyn/cm²	Acid Resistance- MST °C	Scaled	Tukon Hardness KHN	Impact Resistance in./lb
	Linear HDI Oligomer (C in Table 1), Eq. Wt. = 172							
100	72/28 (1/1)	100	0.54	12.0	58	0.75	14	40
	77/23 (1/0.75)	90	0.61	7.3	53	0.72	13	50
	88/12 (1/0.35)	70	0.91	2.3	52	0.66	12	90
140	72/28 (1/1)	Sample Broke During DMA			64	0.76	16	20
	77/23 (1/0.75)	155	0.25	(15.3)	55	0.69	16	20
	88/12 (1/0.35)	80	0.84	2.2	49	0.63	12	50
	Branched HDI Oligomer (E in Table 1), Eq. Wt. = 235							
100	78/22 (1/1)	80	0.57	3.8	58	0.73	10	50
	88/12 (1/0.50)	58	0.96	1.3	55	0.64	6	110
140	78/22 (1/1)	120	0.38	(5.8)	58	0.72	13	30
	88/12 (1/0.50)	66	0.88	1.7	62	0.79	8	50

MF = Monomeric HMMM, I in Table 2; ( ) No minimum observed - values given are at 170°C.

chain carbamate groups which are likely to be less reactive due to steric crowding. The E′ plots are shifted systematically downward in *Figure* 3a as the MF content is reduced. At a weight ratio of 88/12, there is no longer any rise in the E′ plot at higher scan temperatures which suggests that at this MF level, all of the methoxymethyl groups are converted during cure.

The T_g is taken as the temperature of the maximum in the tan δ plot (*Figure* 3b). Increases in MF content cause an increase in T_g and a decrease in tan δ (max). These changes, along with the XLD increase, indicate an increasing extent of cure.[12] In *Figure* 3B, it is evident that the tan δ peak is narrow at 88/12 and that the peak broadens as the Carb/MF weight ratio is changed to 77/23 and 72/28. Broadening is attributed to increasing non-uniformity in network chain length as terminal carbamate groups are used up and methoxymethyl groups then react with more of the sterically hindered mid-chain carbamate groups. Overall, the results of *Figure* 3 support the conclusion that secondary carbamate groups are crosslinked by MF resins.

Data from *Figure* 3 are tabulated in the first three lines of *Table* 4. Values of tan δ (max) and E′(min) indicate that the extent of cure is significant even at the relatively low cure temperature of 100°C. The high value of E′(min) [12.0×10^8 dynes/cm^2] for the 72/28 film is consistent with conversion of some of the mid-chain secondary carbamate groups even at 100°C cure. Property optimization, however, may not call for such high crosslink density. As indicated in the second and third rows of *Table* 4, MF levels well below the stoichiometric ratio can be used to obtain improved flexibility with only moderate losses in hardness. Methyl ethyl ketone (MEK) solvent resistance was also determined, and all films in *Table* 4, including those with less than stoichiometric levels of MF, passed 200 double rubs without film removal or marring. Acid resistance also remains good at reduced levels of MF. It should be noted that commer-

Table 5—MF Cure of Acrylic Carbamate (A) and its Precursor Polyol 30 min; Cure with 0.5 phr pTS

Co-reactant	Cor./MF Wt.	(Eq.)	T_g °C	Tan δ (max)	PW Δ °C	10^{-8} x E' (min) Dyn/cm²	Acid Resistance- MST °C	Scaled	Tukon Hardness KHN	Forward Impact in./lb
100°C Cure										
Acrylic Carbamate	92/8	(1/1)	78	1.22	28	0.89	50	0.69	14	40
	85/15	(1/2)	84	0.90	34	1.49	55	0.64	15	30
Precursor Polyol	90/10	(1/1)	100	0.71	46	2.32	53	0.56	15	30
	82/18	(1/2)	92	0.75	40	2.37	53	0.61	14	30
140°C Cure										
Acrylic Carbamate	92/8	(1/1)	88	0.96	28	1.54	53	0.72	15	40
	85/15	(1/2)	94	0.69	35	2.41	55	0.68	16	40
Precursor Polyol	90/10	(1/1)	111	0.67	32	(2.30)	55	0.56	17	30
	82/18	(1/2)	110	0.54	36	3.44	55	0.57	16	30

MF = Monomeric HMMM, I in Table 2; ( ) No minimum in E'; value given is at 150°C.

cial auto topcoat systems that have been patented for improved acid etch resistance give scaled values of acid resistance in the 0.65 to 0.85 range in the test used here. The minimum spot temperatures (MST) reported in *Table* 4 are also equal to those of formulations patented for etch resistance. The importance of lab tests of acid resistance, however, should not be overstated because it has been reported that outdoor etch and lab results are frequently not in close agreement.[4]

Formulations were also baked at 140°C with results reported in *Table* 4. Higher conversion gave brittle films as indicated by sample breakage during DMA and rather low impact results at 72/28 and 77/23 weight ratios. Films formulated at lower MF levels gave a better balance of properties, but weight ratio and cure temperature were not fully optimized. The hardness and T_g values of the linear HDI films cured at 140°C are higher than those of acrylic polyol/MF auto clearcoats, and the impact resistance range spans that observed for such clearcoats. The purpose here was to prove that MF cure of secondary carbamates is a viable approach for consideration for many potential end uses.

Results are also given in *Table* 4 for films prepared from the branched HDI oligomer, E. Since E has a higher equivalent weight and a lower number of functional groups per molecule than C, we expected crosslink density to be lower, which is consistent with the lower values of E′(min). The branched HDI oligomer, E, is very similar to one of the urethane polyols discussed by Gardon,[5] except for capping of the terminal –OH groups by hexylisocyanate in this work. The acid resistance values of films from the branched oligomer (E) are also very good despite lower XLD and, in the 88/12 examples, much lower T_g values. The good acid resistance of these films, which contain only carbamate/MF crosslinks, is consistent with the suggestion that similar crosslinks contribute to the good acid resistance reported for MF-cured urethane polyols.[5]

Secondary Carbamate Groups or Hydroxyl Groups on the Same Backbone

As shown in *Figure* 1 and *Table* 1, the secondary carbamate co-reactant, A, was prepared by reaction of a commercial acrylic polyol with hexylisocyanate. Co-reactant A and its polyol precursor were crosslinked with a highly monomeric HMMM resin (*Table* 2, I). The development of MEK resistance, as shown in *Figure* 4, clearly indicates that the polyol is more reactive than the secondary carbamate. The cure onset temperature (as defined previously), is below 45°C for the polyol and equal to about 85°C for the corresponding carbamate. The effects of variation in melamine structure on reactivity with hydroxyl groups have been discussed previously,[2,14] and the effects of variation in melamine structure on reactivity with secondary carbamate groups are discussed in the following.

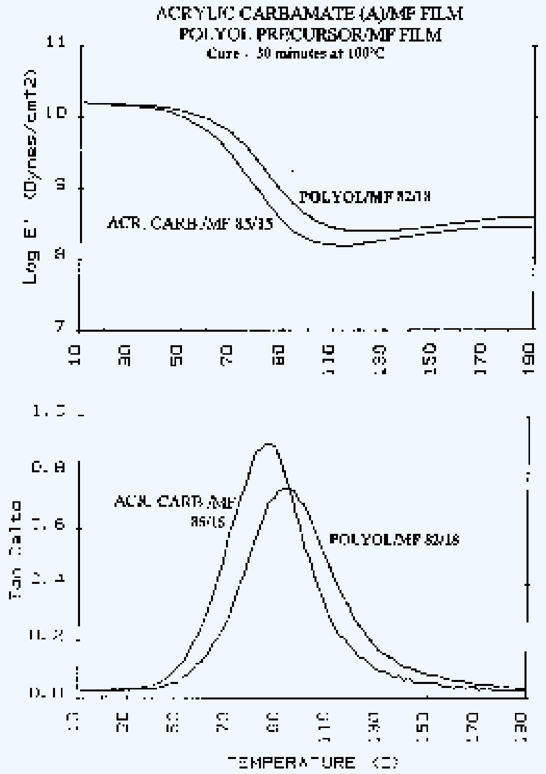


Figure 5—Dynamic mechanical analysis of films from an acrylic carbamate (A) and its polyol precursor: (a) storage modulus, E′, (b) loss tangent, tan δ.

Cure response of the acrylic Carbamate A and its polyol precursor was also compared by DMA. Results are given in *Figure* 5 and *Table* 5. The C6 hydrocarbon chain from hexylisocyanate is expected to internally plasticize the films prepared with the carbamate co-reactant. This effect is clearly evident in the lower T_g values for the carbamate versus the polyol films at both bake temperatures. The height of the tan δ peak [tan δ (max)] and the minimum in storage modulus plot [E′(min)] (*Figure* 5) are useful for comparing cure response of carbamate versus hydroxyl groups. Tan δ (max) decreases and E′(min) increases as the extent of cure increases.[12] At 100°C cure, these measures of cure are quite different for carbamate versus polyol whereas at 140°C cure, the differences are much smaller. We conclude that carbamate groups are less reactive than hydroxyl groups with the methoxymethyl groups from MF. This difference can be observed by DMA at the lower cure temperature (100°C), but when the cure temperature is higher (140°C), the difference in reactivity becomes quite unimportant perhaps because even the slower reacting carbamate groups have reacted nearly to completion. The crosslink densities of these films, as indicated by the E′(min) values,[12] are in the range expected based on complete conversion of carbamate groups or hydroxyl groups. Of course, the C6 chain from hexylmonoisocyanate has a diluting effect on crosslink density so a slightly lower E′(min) is expected for the carbamate versus the polyol co-reactant at equal conversion.

Crosslinking by self-condensation causes strong broadening of the tan peak when acrylic polyol/MF systems are overcured.[12] When self-condensation is forced, peak widths (PW) as high as 75° to 100°C are observed.[12] Peak width values are given in *Table* 5. It is

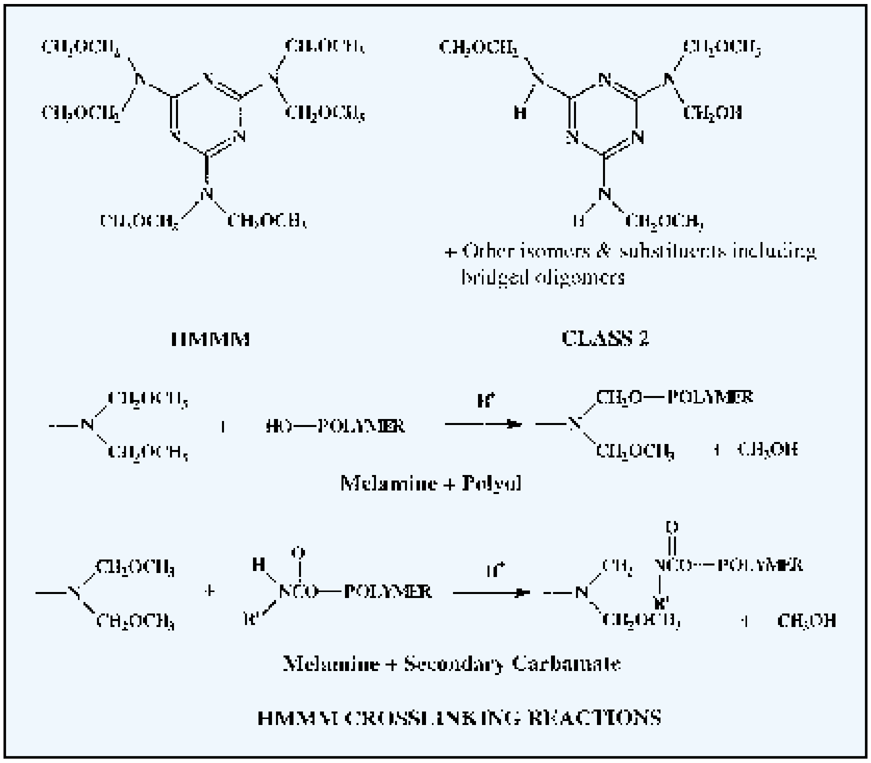


Figure 6—MF structures: hexamethoxymethylmelamine, Class 2 resin (top); proposed cure reactions (bottom).

evident that PW values are low and that those for carbamate cure are no larger than those for polyol cure. This indicates that neither type results in extensive self-condensation. The slight increase in PW going from 1/1 to 1/2 equivalents (co-reactant/MF) indicates that self-condensation of MF is relatively unimportant. The 100°C cure polyol film gives slightly higher PW than the same film cured at 140°C. Higher PW at low cure temperature suggests that the peak is broadened by additional cure during the scan. If self-condensation is the cause of broadening, PW increases with increasing cure temperature.[12]

Results of paint tests are also given in *Table* 5. Hardness and impact results indicate that the carbamate co-reactant has cured to approximately the same extent as the hydroxyl co-reactant. All eight films in this series gave 200+ MEK double rubs, which also indicates a high extent of cure. For this series, paint tests did not distinguish well between the secondary carbamate and its polyol precursor whereas the cure profile method and DMA both revealed the difference in reactivity as discussed previously.

The scaled values of acid resistance in *Table* 5 indicate that the carbamate functional films are more resistant than the polyol films to acid. In contrast, the minimum spot temperature (MST) values show little difference between carbamate and polyol films. Based on poor outdoor etch performance of acrylic polyol/MF clear-coats,[4] larger differences in MST would be expected. However, the polyol films used here differ from commercial auto topcoat types in two respects; the MF content is much lower and the cured film T_g is much higher. Both of these differences are expected[4] to improve the acid resistance of the polyol films. Increasing the cure temperature from 100° to 140°C gives moderate improvement in acid resistance for the carbamate but no improvement for the polyol.

Effect of Melamine Crosslinker Structure on Cure of Secondary Carbamates

Commercial melamine resins are made with a variety of molecular weight distributions, degrees of substitution, and types of etherifying groups.[15] For example, Haseebuddin et al.[16] describe the use of a relatively high molecular weight, butylated MF resin in a crosslink density study with oligourethane diols. Both co-condensation of –OH groups with butoxymethyl groups and self-condensation of the MF crosslinker are reported to contribute to crosslink density. The possibility of reaction between carbamate groups and the MF resin is once again not mentioned, however.

Functional groups present in methylated MF resins are shown in *Figure* 6. Resins that contain relatively high levels of imino groups (–NH) and un-etherified methylol groups (–CH_2OH) have been designated as Class 2 MF resins.[15] The structure of HMMM is also shown in *Figure* 6. Class 1 commercial melamine resins contain more HMMM than the Class 2 resins do. Both classes also contain dimers and higher oligomers in which triazine rings are connected by methylene ether (–NCH_2OCH_2N–) or methylene (–NCH_2N–) bridges.[1, 2] A typical commercial Class 1 MF resin, also referred to as an "HMMM-type" resin, contains 62% monomer, 23% dimer, and 15% trimer and higher oligomers. MF Resin II of *Table* 2, for example, is a Class 1 resin. MF Resins V and VI are examples of Class 2 resins. MF Resin I, prepared by laboratory synthesis, is richer in HMMM than any commercial MF resin.

Table 6—MF Cure of Aqueous Acrylic-Polyurethane Dispersions; Cure—30 min at 100°C, 0.5 phr pTSA

AAPD/MF	T_g	Tan (δ) (max)	10^{-8} x E' at: 25°C	150°C	IPA Resis.	Tukon Hardness	Forward Impact
Wt.	°C		Dynes/cm²		D.R.	KHN	in./lb
100/0	55	0.25	63.	0.8	100	4	160+
90/10	54	0.18	94.	17.	200	5	160+
80/20	50	0.17	126.	33.	200	7	160+

IPA = Isopropanol (all films passed 200 MEK double rubs but with surface marring).
MF = Class 2, VI in Table 2.

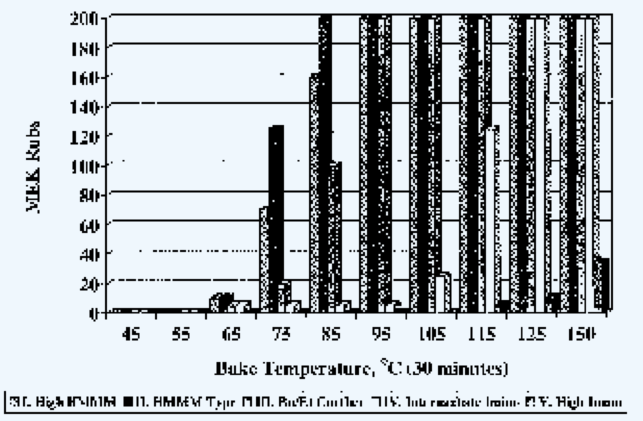


Figure 7—Cure profile data for an acrylic carbamate (A) cured with different types of MF resins. MF/Carbamate A 2/1 by equivalents; catalyst-0.5 phr pTSA; cure time 30 min.

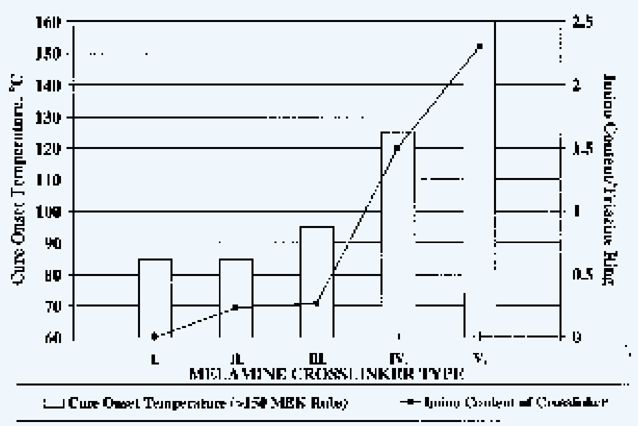


Figure 8—Cure onset temperature and imino content of MF resins. MF/Carbamate A 2/1 by equivalents; catalyst-0.5 phr pTSA; cure time 30 min.

For study of carbamate cure, MF resins were selected to give wide variation in imino content. In the combining ratios of *Table* 2 (M/F/Me/Bu), M is set at 1.0 so that F near 6.0 means low imino and F significantly lower than 6.0 means high imino. MF Resins I through V from *Table* 2 were reacted with the acrylic Carbamate A at a 2.0/1.0 equiv. ratio in the presence 0.5 phr pTSA catalyst. The cure reaction of methoxymethyl groups with hydroxyl groups or secondary carbamate groups is believed to be very similar as shown in the bottom part of *Figure* 6. MEK resistance results from this cure profile study are shown in *Figure* 7. It is evident that the more highly substituted (low NH) etherified melamines are most effective in crosslinking secondary carbamate co-reactants in the presence of strong acid catalysts. The drop in cure response with increasing imino content is rather sharp. Note that no MEK resistance at all is obtained until the cure temperature is raised to 115°C with the MF of highest imino content (V).

In MF cure of hydroxyl-functional co-reactants, it is well established that high imino resins are more reactive than HMMM types.[1, 2] However, the MEK double rub results of *Figure* 7 indicated the opposite effect of imino content for cure of carbamate-functional co-reactants. To demonstrate this surprising imino effect more clearly, cure onset temperature and imino content were plotted together as shown in *Figure* 8. It is evident that cure onset temperature rises sharply with imino content as indicated by the data points obtained for MF resins IV and V. The other MF resins included here all had very low imino content (see *Table* 2), and they all gave much lower cure onset temperature. The reason for the difference in effect of imino groups on reactivity is not fully understood. Possibly steric effects alter mechanistic details. It is evident in *Figure* 6 that steric crowding will be considerably greater at the reaction site for the carbamate co-reactant than for the hydroxyl co-reactant.

The highly monomeric HMMM resin (I) and the commercial HMMM type (II) gave almost identical cure onset temperatures with secondary carbamates. Resin III is a mixed butyl/methyl coetherified resin. It is low in imino content but shows a marginally higher onset temperature than the HMMM types (95°C vs. 85°C). This difference is probably due to the higher boiling point of the butyl alcohol displaced during cure.

MF Cure of Aqueous Polyurethane Dispersions

A possible use for MF/carbamate crosslinking is in modification of films prepared from aqueous polyurethane dispersions (PUDs). The continuing long-term change from solventborne to waterborne coatings has resulted in increased commercial use of PUDs.[17] Improvements in the balance of hardness and flexibility have been reported by novel approaches to coalescence[17] and by combining acrylic and urethane dispersions in a novel hybrid form.[18,19] Although most current uses are in air-dry or forced-dry applications, Blank et al.[20] described

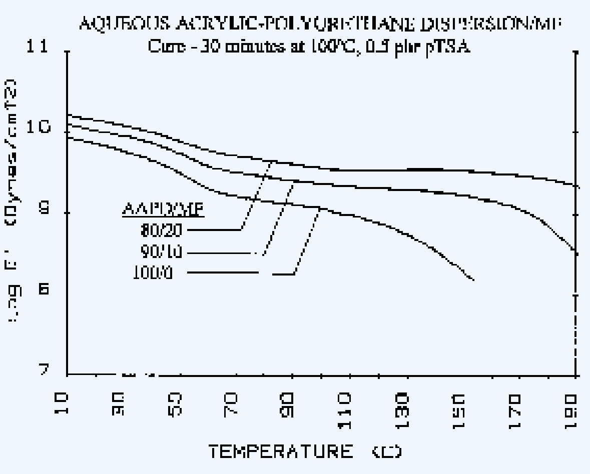


Figure 9—Storage modulus DMA plots showing the effect of adding MF resin to an aqueous acrylic-polyurethane dispersion (AAPD).

improvements in resistance properties obtained by crosslinking the PUDs with amino-formaldehyde resins. The dispersed co-reactants contained carboxyl and/or hydroxyl functional groups for reaction with MF resins. The possibility of reaction of methoxymethyl groups with secondary carbamate groups was not discussed.[20]

Results of using MF Resin VI to crosslink an aqueous acrylic-polyurethane dispersion (AAPD—Flexthane® 610, Air Products and Chemicals, Inc.) are shown in *Figure* 9. DMA plots show that baking for 30 min at just 100°C results in a strong increase in storage modulus (E′). The structure of cured films is clearly quite complex with some evidence of a glass transition in the 40° to 60°C range, but then persistence of high modulus throughout the remainder of the scan all the way to 190°C for the 80/20 AAPD/MF level. These DMA plots are consistent with a non-homogeneous film structure from incomplete coalescence. The hydrophilic shell with a hydrophobic core proposed previously[20] for other PUD systems may be present here as well, but more work would be needed to relate the modulus results to a particular form of non-homogeneity. In this case, the nature of the crosslinking reaction is also not so definite because MF Resin VI is high in imino groups which tend to favor MF self-condensation and disfavor reaction with secondary carbamate groups.

Properties of AAPD/MF films are given in *Table* 6. The effects of MF addition are evident in tabulated E′ values, but T_g values actually decrease slightly with increasing MF content. The tan δ plots (not shown) are very flat with several low, poorly defined peaks. This suggests a very heterogeneous structure with various domains undergoing transition at different temperatures. It appears likely that added MF does not function in the domain that gives rise to the transition in the 50° to 55°C range. Note that the reported tan δ (max) values, associated with these T_g values, are very low. All of the films had good resistance to MEK, but crosslinking by MF improved resistance to isopropyl alcohol (IPA). MF also improved Tukon hardness results sharply without a detectable decrease in impact resistance.

SUMMARY AND CONCLUSIONS

Cure response studies by a gradient oven cure profile method and by DMA indicate that secondary carbamate groups (i.e., urethane groups) react with MF resins at moderate temperatures and that such groups are only slightly less reactive than –OH groups. Use of a series of oligomeric co-reactants resulted in several structure/reactivity conclusions: (1) mid-chain as well as terminal secondary carbamate groups can react, (2) aromatic secondary carbamate groups are slightly less reactive than aliphatic types, and (3) a carbamate co-reactant and its polyol precursor result in similar crosslink density when cured 30 min at 140°C.

Use of a series of MF resins with a selected carbamate co-reactant established that secondary carbamate groups differ from –OH groups in terms of the effect of pattern of substitution on reactivity. For example, high imino content generally increases reactivity of MF resins with –OH groups, but this work indicates that high imino content decreases reactivity with secondary carbamate groups. Results indicate several opportunities for new uses of MF resins: (1) improved acid resistance is observed with carbamate/MF systems versus corresponding hydroxyl/MF systems, (2) it may be cost effective to optimize properties by crosslinking linear urethane prepolymers rather than using polyfunctional isocyanates or polyols to obtain crosslinked urethane networks, and (3) aqueous polyurethane (or acrylic-polyurethane) dispersions may have improved properties when crosslinked by MF resins.

References

(1) Wicks, Z.W., Jr., Jones, F.N., and Pappas, S.P., *Organic Coatings Science and Technology,* Vol. 1, Wiley-Interscience, New York, p. 83, 1992.

(2) Santer, J.O., "Etherified Amino Resins: Synthesis and Reactions in Surface Coatings Applications," *Prog. Org. Coat.*, 12, 309 (1984).

(3) Blank, W.J., "Melamine Formaldehyde Networks with Improved Chemical Resistance," *Proc. ACS PMSE,* 77, 391 (1997).

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

(5) Gardon, J.L., "Polyurethane Polyols: Ester-bond Free Resins for High Solids Coatings," JOURNAL OF COATINGS TECHNOLOGY, *65*, No. 819, 25 (1993).

(6) Walker, F.H. and Gardon, J.L. (to Akzo Nobel Coatings, Inc.), U.S. Patent 5,130,405 (July 14, 1992).

(7) Yahkind, A.L., Wagstaff, I., and Walker, F.H., "Polyurethane Polyols and Coatings Thereof Having Reduced Viscosity," Patent Application by Akzo Nobel N.V., WO 96/40813 (1996).

(8) Rehfuss, J.W. and St. Aubin, D.L. (to BASF Corp.), U.S. Patent 5,356,669 (October 18, 1994).

(9) Swarup, S., McCollum, G.J., Singer, D.L., Olson, K.G., Stefko, S.T., and Mayo, M.A., Internat. Appl. No. PCT/US93/10172 (WO 94/10211) (PPG Industries,) (Oct. 25, 1993).

(10) Ojunga-Andrew, M., Higginbottom, H.P. and Hill, L.W., "High Solids Coatings Based on a Novel Triisocyanate," *Proc. 22nd Waterborne, High-Solids, & Powder Coatings Symp.*, New Orleans, LA, 200, 1995.

(11) Higginbottom, H.P., Bowers, R. G., Hill, L.W., and Courtier, J.F., "Coating Systems Based on Tricarbamate Crosslinkers Derived from Triaminononane,"*Proc. 23rd Internat. Conf. on Organic Coat. Sci. and Technol.*, Athens, Greece, July 7-11, 1997.

(12) Hill, L.W.,"Dynamic Mechanical and Tensile Properties," in *Paint and Coatings Testing Manual*, Ch. 46, pp. 534-546, Koleske, J.V., (Ed.), Fourteenth Edition of Gardner-Sward Handbook, ASTM, Philadelphia, PA, 1995.

(13) Personal communication, Solutia Inc.; Wilson, R.C., Krejsa, M.R., Higginbottom, H.P., and Hill, L.W.

(14) Chu, G. and Jones, F.N., "Low-Temperature Curing Higher-Solids Polyester Coatings with Melamine-Formaldehyde Resin Crosslinkers," JOURNAL OF COATINGS TECHNOLOGY, *65*, No. 819, 43 (1993).

(15) Wicks, Jr., Z.W., Jones, F.N., and Pappas, S.P., *op. Cit.*, p. 89.

(16) Haseebuddin, S., Raju, K.V.S.N., and Yaseen, M., "Crosslink Density and Cure Window of Oligourethane Diol/Melamine High-Solids Coatings," JOURNAL OF COATINGS TECHNOLOGY, *70*, No. 879, 35 (1998).

(17) Satguru, R., McMahon, J., Padget, J.C., and Coogan, R.G., "Aqueous Polyurethanes—Polymer Colloids with Unusual Colloidal, Morphological, and Application Characteristics," JOURNAL OF COATINGS TECHNOLOGY, *66*, No. 830, 47 (1994).

(18) Rynders, R.M., Hegedus, C.R. and Gilicinski, A.G., " Characterization of Particle Coalescence in Waterborne Coatings Using Atomic Force Microscopy," JOURNAL OF COATINGS TECHNOLOGY, *67*, No. 845, 59 (1995).

(19) Hegedus, C.R. and Kloiber, K.A., "Acrylic-Polyurethane Dispersions: Structure and Properties in Industrial Coatings," *Proc. 21st Waterborne, Higher Solids, & Powder Coating Symp.*, New Orleans, LA, 144, February 9-11, 1994.

(20) Blank, W.J. and Tramontano, V.J., "Properties of Crosslinked Polyurethane Dispersions," *Prog. Org. Coat.*, 27, 1 (1996).