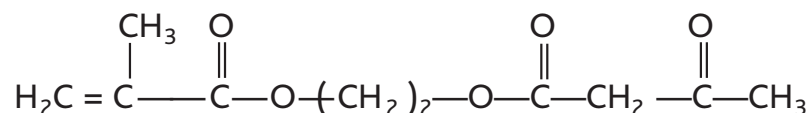


Utility of Eastman™ AAEM (acetoacetoxyethyl methacrylate)

In thermoset coatings



IUPAC: 2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl 3-oxobutanoate
CAS: 021282-97-3

Introduction

The acetoacetyl group offers attractive resin properties and cross-linking versatility to the formulator of thermoset coatings. Lower solution viscosity and glass transition temperature (T_g) have been obtained by adding the acetoacetyl group to the polymer chain. Attractive coatings properties also have been obtained using this group in conventional and nonconventional cross-linking mechanisms. Acetoacetyl chemistry offers the formulator greater latitude for the design of coatings systems.

Eastman™ AAEM is a methacrylic monomer with three sites available for chemical reaction. The methacrylic functionality may be used to react AAEM into an acrylic polymer backbone, leaving an acetoacetyl group pendant to the polymer chain. This pendant group contains the two remaining reactive sites which may be used to add substituents to the polymer or for cross-linking. These sites are the methylene group and the ketone carbonyl. Many of the reactions that can be carried out at these sites are discussed in Eastman publication N-319. This publication discusses 4 reactions involving the acetoacetyl group—reactions with melamines, isocyanates, amines, and a Michael Addition—as cross-linking systems in coatings.

Model resin formulations

To evaluate Eastman™ AAEM in conventional thermoset coatings systems, a series of resins were prepared to compare the cross-linking characteristics of AAEM with those of hydroxyethyl methacrylate (HEMA), the most commonly used hydroxyl-functional acrylic monomer. These were model resin systems using methyl methacrylate (MMA) as the base acrylic monomer and increasing amounts of either AAEM or HEMA as the functionalizing monomer. These resin compositions and their physical properties are described in Table 1.

Table 1 Resin compositions and properties^a

AAEM/MMA copolymers						
Mole % MMA	100	90	80	70	60	40
Mole % AAEM	0	10	20	30	40	60
Wt% Eastman™ AAEM	0	19.2	34.9	47.8	58.8	76.2
M _n , g/mol	9,585	8,818	6,967	7,650	8,930	9,396
M _w , g/mol	50,215	15,697	13,750	22,027	21,437	18,768
T _g , °C	105	84	57	52	44	32
Determined wt% solids	59.0	58.8	57.7	58.0	56.4	56.4
Brookfield viscosity, Pa·s	471	282	42	24	16	6
HEMA/MMA copolymers						
Mole % MMA	100	90	80	70	60	40
Mole % HEMA	0	10	20	30	40	60
Wt% HEMA	0	12.6	25.2	35.8	40.0	66.1
M _n , g/mol	9,585	6,626	7,611	10,056	7,967	9,255
M _w , g/mol	50,215	16,323	16,389	19,423	19,964	23,307
T _g , °C	105	59	69	58	60	—
Determined wt% solids	59.0	62.3	60.8	63.3	63.3	— ^b
Brookfield viscosity, Pa·s	471	1,008	2,016	6,080	9,760	— ^b

^aFormulations presented in this publication are starting points only. Customers must determine for themselves the formulation that best suits their particular needs.

^bIncrease in resin viscosity caused resin to drop out of solution.

Initiator: 1.5% Vazo™ 67 catalyst

Synthesis solvent: Ethyl 3-ethoxypropionate (Eastman™ EEP)

Comparison of Eastman™ AAEM with HEMA in melamine cross-linked enamels¹

To compare the characteristics of AAEM with HEMA as a cross-linking monomer with melamine, the resins listed in Table 1 containing 10, 20, and 30 mole % of the reactive monomers were formulated into melamine cross-linked

enamels as shown in Table 2. A stoichiometric amount of melamine was used for each level of reactive monomer based on the calculated functionality of the resin and assuming an effective functionality of 4 for the melamine.

Table 2 Melamine cross-linked enamel formulations

Mole % Eastman™ AAEM	10	20	30	—	—	—
Mole % HEMA	—	—	—	10	20	30
Enamel composition						
Resin, 60 wt% solids in Eastman™ EEP	190	183	167	190	183	167
Cymel™ 303 melamine resin	10	18	21	11	20	27
Ti-Pure™ R-900 TiO ₂	82	85	81	83	87	85
p-toluenesulfonic acid @ 40 wt% solids	1.5	1.5	1.5	1.6	1.6	1.6
Eastman™ MAK (methyl n-amyl ketone)	27	27	27	27	27	27
Eastman™ DIBK (diisobutyl ketone)	27	27	27	27	27	27
Eastman™ EB	27	27	27	27	27	27
Eastman™ EEP	50	20	14	95	92	137
Enamel constants						
Pigment:binder ratio	40:60	40:60	40:60	40:60	40:60	40:60
Application viscosity, #4 Ford cup, s	39	39	44	37	35	42
Determined wt% solids	47.5	50.5	53.7	45.4	45.8	42.8

The bulky acetoacetyl pendant group provides increased separation between polymer chains in solution, which reduces solution viscosity. Lower solution viscosity is key to obtaining higher-solids coatings. The enamels in Table

2 were adjusted to similar application viscosities, and their solids levels were determined. The enamel systems based on Eastman™ AAEM had consistently higher-solids levels than the corresponding enamels based on HEMA.

¹Color development may occur in acetoacetyl/melamine-containing enamel formulations. Additional information on the suppression of color development is available in Eastman publication N-348.

Cure response

To determine an effective enamel cure schedule for use with the 2 cross-linking monomers, a “cure ladder” study was conducted using the resins containing 20 mole % reactive monomer. The corresponding enamels listed in Table

2 were sprayed on test panels and cured for both 15 and 30 minutes at increasing exposure temperatures as shown in Table 3. An acceptable cure response was indicated by the ability of the coating to pass a 200 MEK double-rub solvent-resistance test.

Table 3 Cure response with melamine cross-linker

Mole % Eastman™ AAEM/HEMA	Cure temperature, °C (°F)	Cure time, minutes	MEK double-rub resistance	Pencil hardness
20% AAEM	107 (225)	15	008	HB
		30	012	F
	121 (250)	15	010	F
		30	012	H
	135 (275)	15	010	H
		30	010	2H
	149 (300)	15	058	4H
		30	200+	5H
	163 (325)	15	200+	7H
		30	200+	7H
20% HEMA	107 (225)	15	024	F
		30	032	H
	121 (250)	15	025	H
		30	037	H
	135 (275)	15	024	2H
		30	050	4H
	149 (300)	15	190	6H
		30	200+	7H
	163 (325)	15	200+	7H
		30	200+	8H

Catalyst level: 0.2 wt% PTSA based on binder.

Substrate: 20-gauge, cold-rolled steel panels with Bonderite™ 37 pretreatment.

The results show that Eastman™ AAEM and HEMA cross-linked effectively with melamine at 149°C (300°F). The HEMA-containing enamel developed better solvent resistance and hardness after 15 minutes exposure at

300°F than the Eastman™ AAEM-based system, thus indicating a somewhat faster cure response. Both enamels showed good cure after 30 minutes exposure at 300°F, and this cure schedule was chosen for the more complete enamel evaluation.

Performance comparison

To compare the performance of cross-linking through Eastman™ AAEM or HEMA, the 6 enamels listed in Table 2 were sprayed on test panels, cured, and evaluated as shown in Table 4.

Table 4 Melamine cross-linked enamel properties^a

Mole % Eastman™ AAEM	10	20	30	—	—	—
Mole % HEMA	—	—	—	10	20	30
Average film thickness, μm (mil)	25 (1.0)	25 (1.0)	25 (1.0)	25 (1.0)	25 (1.0)	25 (1.0)
Gloss @ 60°/ 20°	88/71	93/73	88/66	87/68	88/71	83/62
Pencil hardness to mar	7H	7H	9H	7H	6H	9H
Impact resistance, N·m (in.-lb)						
Direct	2.5 (22)	1.8 (16)	1.4 (12)	2.3 (20)	2.3 (20)	2.0 (18)
Reverse	0.2 (2)	0.2 (2)	0.2 (2)	0.2 (2)	0.2 (2)	0.2 (2)
3.2 mm (1/8 in.) Conical mandrel	Fail	Fail	Fail	Fail	Fail	Fail
Stain resistance ^b						
Iodine after 5 min	N	N	N	N	N	VS
30 min	S	S	M	S	M	S
Ink after 24 h	M	M	M	M	M	M
Mustard after 24 h	N	N	N	N	N	N
Shoe polish after 24 h	N	N	N	N	N	N
Chemical resistance ^b						
Sulfuric acid after 1 h	N	N	N	N	N	N
Sodium hydroxide after 1 h	N	N	N	N	N	N
Cleveland humidity after 48 h @ 60°C (140°F)						
% Gloss retention @ 60°/20°	99/99	98/94	97/94	100/95	99/97	99/87
Blisters	None	None	None	None	None	None
Salt spray after 500 h						
Blisters	None	None	None	None	None	None
Creepage from scribe, mm (in.)	<1.6 (<1/16)	1.6 (1/16)	<1.6 (<1/16)	6.4 (1/4)	6.4 (1/4)	6.4 (1/4)
Weatherability after 500 h						
% Gloss retention by carbon arc @ 60°/20°	81/59	90/79	54/35	95/80	90/68	43/30
QUV-B ^c accelerated weathering test @ 60°/20°	94/92	92/84	92/78	97/90	91/77	98/87

^aCure schedule: 30 minutes @ 149°C (300°F)

^bScale: N—No effect, VS—Very slight effect, S—Slight effect, M—Moderate effect

^cQ-Panel Company

Substrate: 20-gauge, cold-rolled steel panels with Bonderite™ 37 pretreatment.

Some of the performance data, particularly hardness and impact values, are heavily influenced by the large amount of MMA in these model resin systems. Comparison of the data, however, shows little difference in enamel performance between the Eastman™ AAEM- and the HEMA-containing systems. This further confirms that AAEM does cross-link effectively with melamine under these cure conditions.

There was a difference in performance between the two systems in their salt-spray resistance. While none of the

coatings showed any blistering, the Eastman™ AAEM-based coatings had less creepage from the scribe than the HEMA-containing systems. This creepage is influenced by the corrosion resistance of the coating and its adhesion to the substrate. AAEM has been shown in other systems to chelate with metals, thus improving polymer adhesion to metal substrates. This improved adhesion is believed to have resulted in the reduced salt-spray creepage for the AAEM-based coatings.

Shelf stability of Eastman™ AAEM acrylic—melamine enamels

The acetoacetyl group will react not only with melamines but with the free formaldehyde present in commercially available melamine cross-linkers as well. This reaction with formaldehyde occurs very rapidly at the methylene group site at room temperature and, because both the acetoacetyl and the formaldehyde will react twice, constitutes a cross-linking reaction. This reaction has been shown to limit the shelf stability of an acetoacetyl-melamine coating system. For example, acetoacetate resin-based coatings that use Cymel™ 303 cross-linker (0.5 wt% formaldehyde) tend to gel in about 49 days at ambient temperature. Coatings that contain 2.0 wt% (or more) formaldehyde in the melamine gel in less than 24 hours. One possible solution to this problem is the use of Eastman™ EAA (ethyl acetoacetate) as a formaldehyde-scavenging additive to extend shelf life.

To test this theory, coatings containing 2.0 wt% formaldehyde in melamine were made with the addition of Eastman™ EAA in 1:1, 2:1, and 3:1 molar ratios of EAA to formaldehyde. A coating with 0.5 wt% formaldehyde was also made with the addition of a 1:1 molar ratio of EAA to formaldehyde. Formulations for these coatings are given in Table 5.

Table 5 Effect of Eastman™ EAA on shelf stability

Wt% free formaldehyde in melamine	0.5	2.0	2.0	2.0
Molar ratio, EAA:formaldehyde	1:1	1:1	2:1	3:1
Components	Weight, g			
20 mole % Eastman™ AAEM acrylic @ 60 wt% solids in Eastman™ EEP	100.0	100.0	100.0	100.0
Cymel™ 303 melamine resin ^a	25.7	25.32	25.32	25.32
Formaldehyde (added)	0	0.38	0.38	0.38
Eastman EAA	1.2	4.4	8.8	13.2
Solvent blend ^b	50.0	50.0	50.0	50.0

^aCymel™ 303 contains 0.5 wt% free formaldehyde.

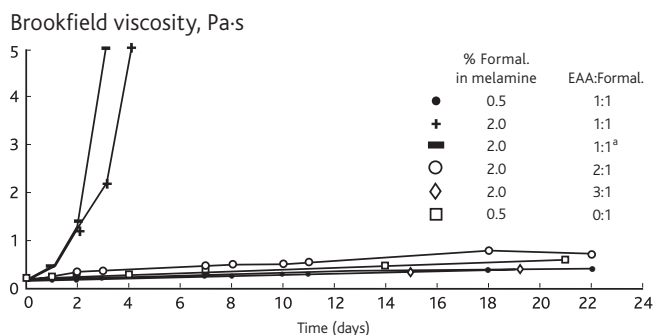
^bSolvent blend: 70/15/15 Eastman™ MAK / Eastman™ EEP / n-BuOH

The shelf life of these coatings was measured by taking daily Brookfield™ viscosity readings. Results are shown in Figures 1 and 2.

Use of Eastman™ EAA in the 0.5% formaldehyde sample extended the shelf life from the original 49 days to 90 days. The addition of EAA in a 3:1 molar ratio extended the shelf life from less than 24 hours to 74 days.

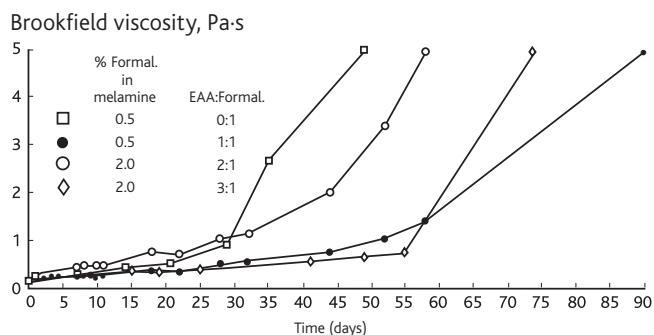
Use of EAA as a formaldehyde scavenger appears to be a very useful method for extending the shelf life of acetoacetate-melamine coatings systems. This also offers the added benefit of reducing the amount of formaldehyde emitted from the coating during cure.

Figure 1
Acetoacetate/melamine cross-link effect of Eastman™ EAA on shelf life



*EAA added to grind

Figure 2
Acetoacetate/melamine cross-link effect of Eastman™ EAA on shelf life (extended)



Comparison of Eastman™ AAEM with HEMA in isocyanate cross-linked enamels

To compare the characteristics of Eastman™ AAEM with HEMA as a cross-linking monomer with isocyanates, the resins listed in Table 1 containing 10, 20, and 30 mole % of the reactive monomers were used to formulate the

enamels shown in Table 6. A stoichiometric amount of a blocked isocyanate was used with each resin. These enamels were sprayed on test panels, cured, and evaluated as shown in Table 7.

Table 6 Isocyanate cross-linked enamel formulations

Mole % Eastman™ AAEM	10	20	30	—	—	—
Mole % HEMA	—	—	—	10	20	30
Enamel composition						
Resin, 60 wt% solids in Eastman™ EEP	155	133	117	170	125	106
Desmodur™ BL-3175 resin	41	64	77	30	70	86
Ti-Pure™ R-900 TiO ₂	83	85	85	83	85	85
Fascat™ 4202 catalyst	0.6	0.6	0.6	0.6	0.6	0.6
Eastman™ MAK	27	27	27	27	27	27
Eastman™ DIBK	27	27	27	27	27	27
Eastman™ EB	27	27	27	27	27	27
Eastman™ EEP	—	15	15	145	92	90
Fluorosurfactant flow aid	0.6	0.6	0.6	0.6	0.6	0.6
Enamel constants						
Pigment: binder ratio	40:60	40:60	40:60	40:60	40:60	40:60
Application viscosity, #4 Ford cup, s	28	28	28	23	25	23
Determined wt% solids	47.3	51.5	51.1	46.0	45.2	43.6

Table 7 Isocyanate cross-linked enamel properties^a

Mole % Eastman™ AAEM	10	20	30	—	—	—
Mole % HEMA	—	—	—	10	20	30
Average film thickness, μm (mil)	33 (1.3)	25 (1.0)	25 (1.0)	30 (1.2)	23 (0.9)	25 (1.0)
Gloss @ 60°/20°	97/83	78/54	84/66	96/80	89/73	87/68
Pencil hardness to mar	8H	8H	8H	8H	8H	8H
Impact resistance, N·m (in.-lb)						
Direct	2.3 (20)	2.3 (20)	2.9 (26)	2.3 (20)	2.9 (26)	2.9 (26)
Reverse	<0.2 (<2)	<0.2 (<2)	<0.2 (<2)	<0.2 (<2)	<0.2 (<2)	0.2 (<2)
3.2 mm (1/8 in.) Conical mandrel	Fail	Fail	Fail	Fail	Fail	Fail
MEK double-rub resistance						
Number passed	200+	200+	200+	200+	200+	200+
Stain resistance ^b						
Iodine after 5 min	N	N	VS	N	N	N
Iodine after 30 min	N	M	SEV	N	S	SEV
Ink after 24 h	SEV	SEV	SEV	M	M	SEV
Mustard after 24 h	N	N	N	N	N	N
Shoe polish after 24 h	N	N	N	N	N	N
Chemical resistance ^b						
Sulfuric acid after 1 h	N	N	N	N	N	N
Sodium hydroxide after 1 h	N	N	N	N	N	N
Cleveland humidity after 48 h @ 60°C (140°F)						
% Gloss retention @ 60°/20°	100/100	100/100	100/100	100/100	100/100	100/100
Blisters	None	None	None	None	None	None
Salt spray after 500 h						
Blisters	None	None	None	None	None	None
Creepage from scribe, mm (in.)	<1.6 (<1/16)	<1.6 (<1/16)	<1.6 (<1/16)	<1.6 (<1/16)	<1.6 (<1/16)	<1.6 (<1/16)
Weatherability after 500 h						
% Gloss retention by QUV-B accelerated weathering test @ 60°/20°	100/100	100/100	97.6/100	98.9/100	98.9/100	100/00

^aCure schedule: 30 minutes @ 149°C (300°F)

^bScale: N—No effect, VS—Very slight effect, S—Slight effect, M—Moderate effect, SEV—Severe effect

Substrate: 20-gauge, cold-rolled steel panels with Bonderite™ 37 pretreatment.

There was no significant difference in the performance data between the Eastman™ AAEM- and HEMA-based coatings systems. These results indicate that the

acetoacetyl group can be an effective functionality for cross-linking with isocyanates.

Alternative cross-linking mechanisms

The previous discussion described the coatings performance of melamine and isocyanate cross-linking through the acetoacetyl group. One of the values of acetoacetyl chemistry is its versatility in providing alternative cross-linking mechanisms. Two of these will be discussed: the Michael Reaction and enamine cross-link.

Michael Reaction

The Michael Reaction offers coatings formulators another option in ambient-temperature or low-temperature, cross-linking systems. Completion of this reaction requires a strong base catalyst. The basicity of the catalyst influences both cure time and pot life of this two-component system. Catalysts for this reaction are discussed in other literature.¹ The catalyst selected for this work was 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) because of its attractive combination of pot life and cure time.

Table 8 Michael Reaction cross-linked enamel formulations

Mole % Eastman™ AAEM	20	30
Part A—grind		
Resin at 60 wt% solids in Eastman™ EEP	43.6	32.6
Trimethylolpropane triacrylate	3.6	4.3
Ti-Pure™ R-900 TiO ₂	20.4	15.2
Eastman™ MIAK	14.4	17.8
Eastman™ EEP	7.9	14.4
<i>n</i> -Butyl alcohol	7.9	14.4
Part B—catalyst		
DBU at 5 wt%	2.2	1.3
Total—Parts A and B	100.0	100.0
#4 Ford cup viscosity, s	30	32

Coatings performance

The coatings performance of the Eastman™ AAEM-based enamels listed in Table 8 was evaluated after curing 7 days at ambient temperature, and the results are shown in Table 9. The data shows good overall coatings performance, particularly with respect to stain resistance. This indicates that the Michael Reaction can have utility as an alternative cross-linking system for coatings.

Table 9 Michael Reaction cross-linked enamel properties^a

Mole % Eastman™ AAEM	20	30	
Average film thickness, μm (mil)	30 (1.2)	30 (1.2)	
Gloss @ 60°/20°	83/74	82/70	
MEK double-rub resistance			
Number passes	250	250	
Pencil hardness to mar	4H	3H	
Impact resistance, N-m (in.-lb)			
Direct	0.9 (8)	2.0 (18)	
Reverse	0.5 (4)	0.5 (4)	
Stain resistance ^b			
Iodine after	5 min	N	N
	30 min	N	VS
Ink after 24 h	N	N	
Chemical resistance ^b			
Sulfuric acid after 1 h	N	N	
Sodium hydroxide after 1 h	N	N	

^aCure schedule: 7 days at ambient temperature.

^bScale: N—No effect, VS—Very slight effect, S—Slight effect, M—Moderate effect

Substrate: 20-gauge, cold-rolled steel panels with Bonderite™ 37 pretreatment.

Hydrolytic stability

As previously stated, Michael Reaction cross-link requires the presence of strong base catalysts, and the most effective catalysts remain in the coating film after ambient-temperature cure. This alkaline material can also catalyze hydrolysis of the film, limiting hydrolytic stability. A study was undertaken to evaluate the utility of a relatively low-temperature bake schedule in overcoming this hydrolytic stability problem.

The coatings systems used to evaluate enamel performance properties of the Michael Reaction were again used for this study. The coatings were sprayed onto metal substrates and subjected to temperatures ranging from 80° to 140°C (176° to 284°F), at times of 15 to 60 minutes. These panels were exposed in a Cleveland humidity cabinet and evaluated after 2 hours and 24 hours (Table 10).

¹Clemens, R. J., "A Comparison of Catalysts for Cross-linking Acetoacetylated Resins via the Michael Reaction," *Proceedings of the 15th Waterborne and Higher-Solids Coatings Symposium, New Orleans, La., Feb. 1988.*

Table 10 Cleveland humidity resistance Michael Reaction cross-linked enamel performance rating^a

Bake time, min	Humidity exposure time			
	20 Mole % Eastman™ AAEM		30 Mole % Eastman™ AAEM	
	2 h	24 h	2 h	24 h
@ 80°C (176°F)				
15	3	1	3	1
30	3	1	3	1
45	3	1	3	1
60	3	1	3	1
@ 100°C (212°F)				
15	6	1	8	2
30	8	1	8	4
45	9	5	10	8
60	10	7	10	8
@ 110°C (230°F)				
15	6	1	9	2
30	8	5	10	6
45	9	8	10	8
60	10	9	10	9
@ 120°C (248°F)				
15	6	6	9	6
30	9	8	10	9
45	10	9	10	9
60	10	9	10	10
@ 140°C (284°F)				
15	9	8	9	8
30	10	9	10	9
45	10	10	10	10
60	10	10	10	10

^aRating scale: 10—No effect, 1—Severe effect

As the data shows, the bake schedules that yield coatings with acceptable humidity resistance are:

- 110°C (230°F), 45–60 minutes
- 120°C (248°F), 30–45 minutes
- 140°C (284°F), 15–30 minutes

Some lower bake schedules eliminated blistering under humidity exposure, but discoloration (darkening) of the films did occur.

Pot life

Since pot life depends on concentration of catalyst and acetoacetyl functionality, a study was undertaken to measure the specific influence of these variables on pot life. Acrylic copolymers containing 20 and 30 mole % Eastman™ AAEM (Table 1) were selected for this study. Coatings were prepared from both resins using trimethylolpropane triacrylate cross-linker and 4 levels of DBU catalyst (Table 8). The pot life of each system was determined by hourly viscosity measurements (Figures 3 and 4). For the resin containing 20 mole % Eastman™ AAEM, 2 mole % DBU gave a pot life of greater than 9 hours, while 1 mole % DBU gave the same results in the 30 mole % Eastman™ AAEM resin. Both of these systems cured at ambient temperature within 72 hours to pass 250 MEK double rubs. These catalyst levels were used for the remainder of the Michael Reaction evaluations.

Figure 3
Michael addition, DBU catalyst 20 mole % Eastman™ AAEM resin, pot life

Brookfield solution viscosity, mPa·s

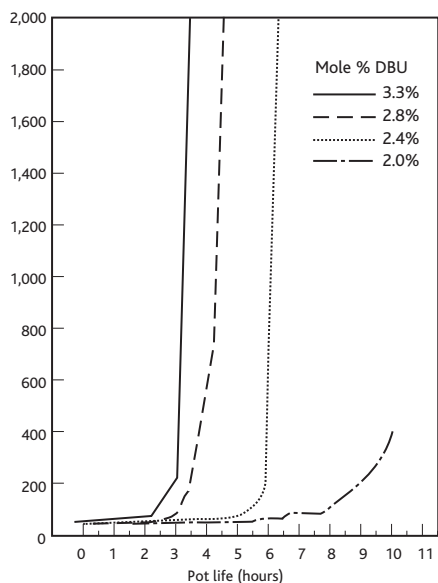
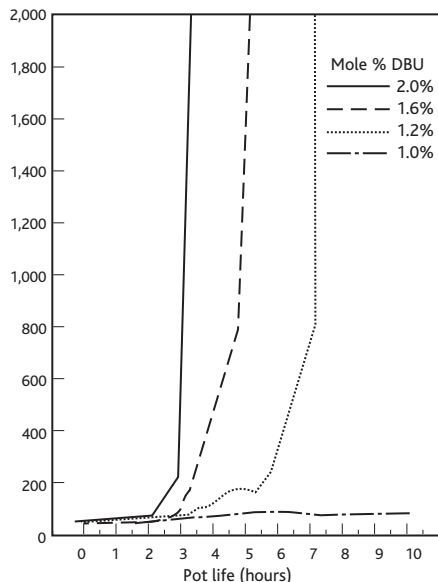


Figure 4
Michael addition, DBU catalyst 30 mole % Eastman™ AAEM resin, pot life

Brookfield solution viscosity, mPa·s



Enamine formation

Another mechanism for cross-linking through the acetoacetyl functionality is the reaction of the enolic hydroxyl with polyfunctional amines to form enamine structures. This is a rapid reaction at ambient temperatures that proceeds without a catalyst.

This cross-linking reaction was evaluated using 20 and 30 mole % Eastman™ AAEM based copolymers (Table 1) cross-linked with 1,6-hexanediamine (Table 11). The pot life of this two-component system was about 1 hour, and within 72 hours, the coating had developed sufficient cure to withstand 250 MEK double rubs. The choice of a more sterically-hindered amine can extend the pot life of the system.

Table 11 Enamine cross-linked enamel formulations

Mole % AAEM	20	30
Part A—grind		
Resin @ 60 wt% in Eastman™ EEP	52.3	51.4
Ti-Pure™ R-900 TiO ₂	22.9	23.2
Fluorosurfactant flow aid @ 20 wt%	0.9	0.9
Diacetone alcohol	5.2	5.1
Eastman™ MIBK	5.2	5.1
Eastman™ EEP	10.5	10.3
Part B—cross-linker		
1,6-Hexanediamine	3.0	4.0
Total: Parts A and B	100.0	100.0

Coatings performance

Coatings performance of the Eastman™ AAEM-based enamels in Table 11 was evaluated after 7 days at ambient temperature. The results are shown in Table 12. From the limited testing done thus far, this appears to be a viable cross-linking mechanism for ambient-temperature-cure coatings.

Table 12 Enamine cross-linked enamel properties^a

Mole % Eastman™ AAEM	20	30
Average film thickness, μm (mil)	38 (1.5)	38 (1.5)
Gloss @ 60°	57	57
Pencil hardness	2H	2H
Impact resistance, F/R, N·m (in.-lb)	2.5/0.1 (22/1)	2.5/0.1 (22/1)
MEK double-rub resistance Number passed	250+	250+
Stain resistance ^b		
Iodine after		
5 min	N	M
30 min	M	M

^aCure schedule: 7 days at ambient temperature.

^bScale: N—No effect, VS—Very slight effect, S—Slight effect, M—Moderate effect

Substrate: 20-gauge, cold-rolled steel with Bonderite™ 37 pretreatment.

Pot life and cure control

Pot life and cure speed of an enamine cross-link reaction may be affected by several factors. The most pronounced effects come from:

- Choice of amine
- Solvent selection
- Resin molecular weight

The following data shows the effects observed from these 3 factors.

Choice of amine. Numerous amine cross-linkers were evaluated in this reaction, and the type of amine used was found to be very important in achieving a useful combination of pot life and cure speed.

For example, primary amines offer very rapid cure after application. However, the pot life of these systems is limited, ranging from 0.5 to 2 hours. Secondary amines give very long pot life in these coatings, but the cure time is also very long. Tertiary amines will not participate in the enamine formation reaction.

The best compromise for achieving good pot life and cure speed appears to be the use of cross-linkers that contain primary amines that are pendant to secondary carbons. These materials offer reactivity that is low enough to give useful pot life (about 9 hours) and very rapid cure (100–250 MEK double-rub resistance within 24–48 hours).

Versamine™ C-30, an amine similar to that described above, was used for the remainder of these evaluations.

Solvent selection. Experience has shown that in epoxy coatings the use of a ketone solvent in conjunction with an amine cross-linker will extend the pot life of the system. The ketone reacts in situ with the amine to form the imine (ketamine), thereby effectively blocking the cross-linker.

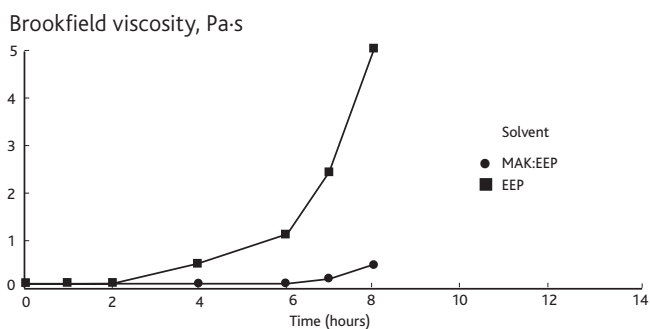
Evaluations show that this effect is also observed in the enamine reaction. Two coatings were formulated based on an 80:20 molar ratio MMA: Eastman™ AAEM acrylic resin and using Versamine™ C-30 as the cross-linker. One coating used only Eastman™ EEP as the solvent. The second used a 2:1 blend of Eastman™ MAK: Eastman™ EEP. The formulations for these coatings are shown in Table 13.

Table 13 Effect of ketone solvent on pot life enamel formulations

Solvent system	Eastman™ EEP	2:1 Eastman™ MAK:EEP
Components	Weight, g	
Part A		
80:20 MMA:Eastman™ AAEM acrylic @ 60 wt% solids in EEP	333.3	333.3
Ti-Pure™ R-900 TiO ₂	133.4	133.4
Eastman™ EEP	100.0	—
2:1 Eastman™ MAK:EEP	—	100.0
Part B		
Versamine™ C-30 amine	42.7	42.7

Viscosity of these coatings was measured hourly to determine pot life. Results are shown in Figure 5.

Figure 5 Enamine cross-link solvent effect on pot life



As the data indicates, use of a ketone solvent extended the useful pot life of this system from about 4 hours to slightly more than 8 hours. Both coatings exhibited cure in excess of 200 MEK double-rub resistance within 24 hours.

Resin molecular weight. The pot life of two-package systems is affected by the molecular weight (Mn) of the coating resin. As the resin molecular weight increases, the number of cross-link reactions required to achieve gel decreases. This effect is also observed in enamine formation cross-link.

A series of 80:20 molar ratio MMA: Eastman™ AAEM acrylic resins was produced for these tests. The synthesis temperature of the cooks was varied to give variation of Mn. All other synthesis parameters were held constant. The synthesis temperatures and resultant molecular weights are given in Table 14.

Table 14 Acrylic resin synthesis temperature vs. molecular weight

Temperature, °C (°F)	Number average molecular weight, g/mol
70 (158)	11,200
100 (212)	9,200
130 (266)	5,300
160 (320)	3,200

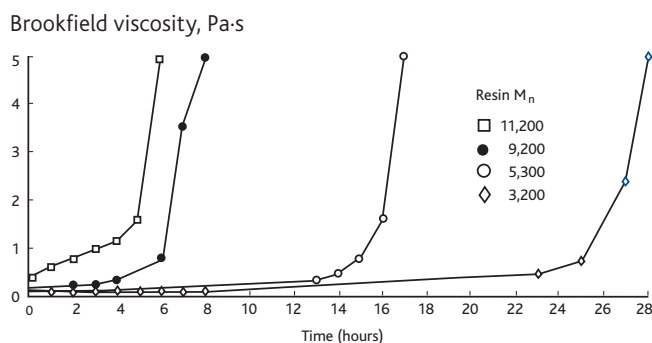
The resins were formulated into enamine cross-linked enamels using the formulation given in Table 15.

Table 15 Coating formulation effect of resin molecular weight on coating pot life

Components	Weight, g
Part A 80:20 Molar MMA: Eastman™ AAEM acrylic @ 60 wt% solids in Eastman™ EEP	166.7
Ti-Pure™ R-900 TiO ₂	79.5
2:1 MAK:EEP blend	120.0
Part B Versamine™ C-30 amine	19.3

The pot life of each of these coatings was evaluated by hourly Brookfield viscosity measurement. The results are shown in Figure 6.

Figure 6 Enamine cross-link resin M_n effect on pot life



The molecular weight of the resin used has a dramatic effect on the pot life of an enamine cross-linked coating. The highest M_n resin (11,200) gave the shortest pot life, while the resin having a 3,200 Mn gave a very long pot life. Resins for this type of coating should be carefully formulated to give the combination of pot life and cure speed desired.

Care should be taken in the use of amines as coatings cross-linkers. As with any other alkaline material, the presence of free amines in the coating film can cause hydrolysis of the film with exposure to moisture. An excess of acetoacetyl functionality should be incorporated to ensure complete reaction of the amine groups.

Summary

Acetoacetyl chemistry has been shown to offer numerous benefits to the coatings formulator. The viscosity reduction it provides allows the production of resins for high solids, low VOC compliance coatings. The two reactive sites can be used for reaction with conventional cross-linkers—melamines and isocyanates—to achieve attractive properties. Further, the reactivity of these two sites will allow the use of nonconventional cross-linking mechanisms that provide ambient temperature nonisocyanate cure. The acetoacetyl group offers versatility in meeting present and future needs of the coatings industry.

Raw material suppliers

Bonderite™ 37	Henkel
Cymel™ 303 resin	Cytec
Desmodur™ BL-3175 resin	Bayer Material Science
Fascat™ 4202 catalyst	Arkema, Inc.
Trimethylolpropane triacrylate	Sartomer
Ti-Pure™ R-900 TiO ₂	DuPont
Vazo™ 67 catalyst	DuPont
Versamine™ C-30 amine	BASF



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