Amine-Functional Curatives for Low Temperature Cure Epoxy Coatings

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An active area of technology development is the design of improved epoxy/amine binder systems for low temperature cure coatings. Low temperature cure epoxy coatings allow applicators to extend the painting season because coatings can be applied even when the temperature falls below 50°F. This paper begins with a basic overview of the curing agent technologies available for low temperature epoxy/amine coatings. The coatings performance of several low temperature curatives with standard liquid epoxy resin is studied in this work. Differential scanning calorimetry is used to monitor the binder systems' cure rate at 40°F over a 14-day period. The coatings performance in clear varnish formulations is presented; cured at standard ambient conditions (77°F, 55% RH) and at sub-ambient, high humidity conditions (50°F, 90% elative humidity and 40°F, 80% relative humidity). This study concludes with evaluation of a new approach to low temperature cure epoxy coatings. This approach uses low temperature curatives in combination with polyacrylated epoxy resins. The results show that these new binder systems give improved clarity, blush resistance, and cure development under low temperature, high humidity conditions.

INTRODUCTION

In today's marketplace, formulators of epoxy/amine coatings face the challenging dual task of meeting VOC regulations and improving the coatings' cost/performance ratio relative to historical industry standards. Traditional epoxy/polyamide coatings have served the industry well for more than 40 years but newer curative technologies eliminate some of the polyamides' well-known limitations. In recent years, these new technologies have led to specialty amine hardeners for low temperature epoxy coatings. Low temperature cure coatings allow applicators to extend the painting season into the fall and early winter months because coating application can continue even when the temperature falls below 50°F.

This paper provides an overview of the curative technologies for low temperature epoxy coatings. The coatings performance of four low temperature amine curatives in unpigmented films is determined. Differential scanning calorimetry (DSC) is used to monitor the cure rate of these binder systems. This study concludes with an evaluation of a new approach to low temperature epoxy/amine formulations. This approach uses low temperature curatives in combination with polyacrylated epoxy resins. This new approach gives improved clarity, blush resistance, and cure development under low temperature, high humidity conditions. The one drawback is that pot lives for these new systems are very short.

ROUTES TO LOW TEMPERATURE CURE COATINGS

Epoxy/Amine Accelerators

One technology for speeding dry times and increasing the cure rate of epoxy/amine coatings for low temperature (≤50°F) applications is to accelerate the epoxy/amine reaction.[1] A simplified epoxy/amine reaction is shown in *Reaction* 1.

Several classes of chemicals accelerate this crosslinking reaction. These chemical classes include: organic acids[2] (e.g., salicylic or benzoic), tertiary amines[3] (e.g., BDMA - benzyl dimethyl amine or tris-2,4,6 dimethylaminoe-methyl phenol), alcohols (e.g., methanol), water, alkyd-substituted phenols[4] (e.g., nonylphenol, bisphenol A) and primary aliphatic amines[2] (e.g., DETA - diethylenetriamine, TETA - triethylenetetramine). The amount of accelerator required for acceptable cure rate depends on the specific chemical chosen and the concentration of active accelerator in the final formulation.

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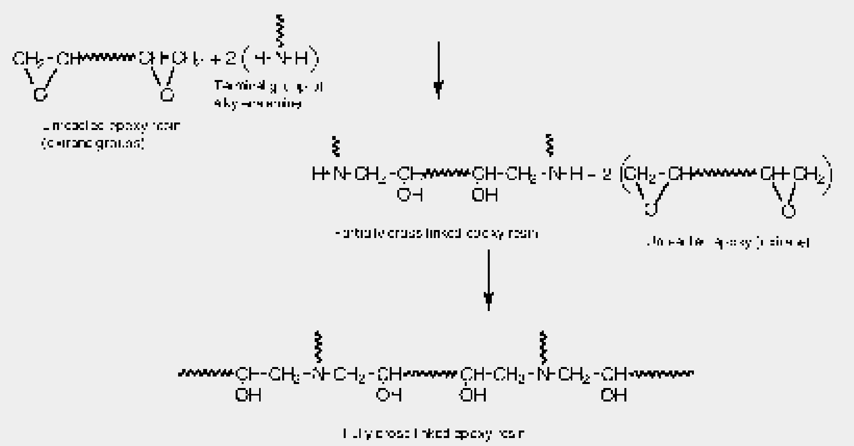


Reaction 1: Simplified epoxy/amine reaction.

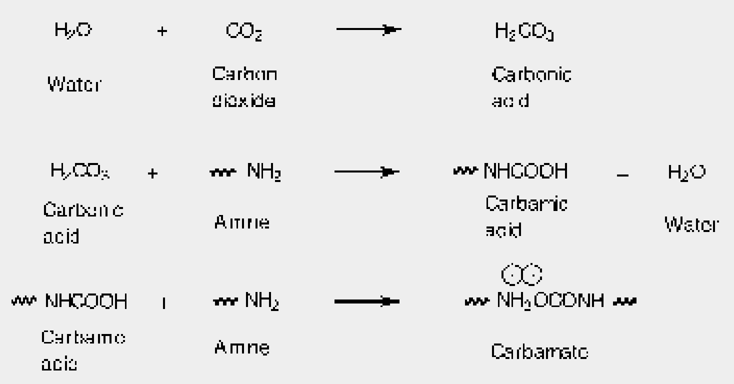
The traditional workhorse of amine curatives is the polyamidoamines (or polyamides). Polyamides find applications in such diverse coatings areas as marine, industrial maintenance, water storage and treatment, pulp and paper, equipment finishes and transportation coatings. Polyamides are made by reacting dimer fatty acid with multifunctional ethylene amines such as DETA or TETA. Polyamides are generally not recommended for application at temperatures below 55°F because of their slow reactivity.[5] Acceptable cure rates at lower temperatures (45-50°F) are possible if the epoxy/polyamide is accelerated with phenolic tertiary amines such as tris-2,4,6-(dimethylaminomethyl) phenol.[5,6] However, accelerator levels in the film must be minimized if maximum coating performance (e.g., water-, corrosion- and chemical-resistance) are to be maintained. Shorter pot life is another disadvantage of accelerating epoxy/polyamide coatings.

Modified Amine Adducts

In addition to meeting dry time and cure rate requirements, low temperature amine curing agents must be designed for blush and water spot resistance. Primary amines react with atmospheric carbon dioxide and water to form carbamates that can exude to the surface and produce blush.[7] The formation of blush (sometimes called blooming or exudate) usually has a detrimental effect on coating performance because it can lead to gloss reduction, increased yellowing, poor recoatability, and intercoat adhesion problems. Low temperature, high humidity conditions increase the probability of blush formation. The chemical reactions which lead to carbamate formation are found in *Reaction* 2.

To minimize carbamate formation and improve early water spot resistance, curing agent manufacturers have developed a wide variety of modified amine adducts. These adducts reduce or eliminate blush formation because the primary amine hydrogens are prereacted with epoxide groups. Amine adducts are prepared by reacting excess primary amines with epoxy resin.[8] The reaction between liquid epoxy resin and an aliphatic polyamine is shown in *Reaction* 3.

A wide variety of amine curatives and epoxy resins are utilized for amine adduct reactions.[9] Some of the most common aliphatic and cycloaliphatic amines include:[10] diethylenetriamine (DETA), triethylene tetramine (TETA), tetraethylene pentamine (TEPA), isophorone diamine (IPDA), bis-para-aminocyclohexyl methane (PACM), and 1,2-diaminocyclohexane (1,2-DACH). The epoxy resins range from liquid epoxy resins through solid epoxy resins. Since the amine adduct reaction increases molecular weight, these products are less corrosive and less volatile than their unmodified amine precursors. Most importantly, amine adducts are less susceptible to blush formation so they are well-suited for low temperature cure coatings. However, these advantages come with a significant increase in curative viscosity. To lower viscosity, amine adducts are cut with solvents or modified with plasticizers (such as benzyl alcohol). For low temperature cure, amine adducts are often accelerated to speed property development in the final coating.[11]



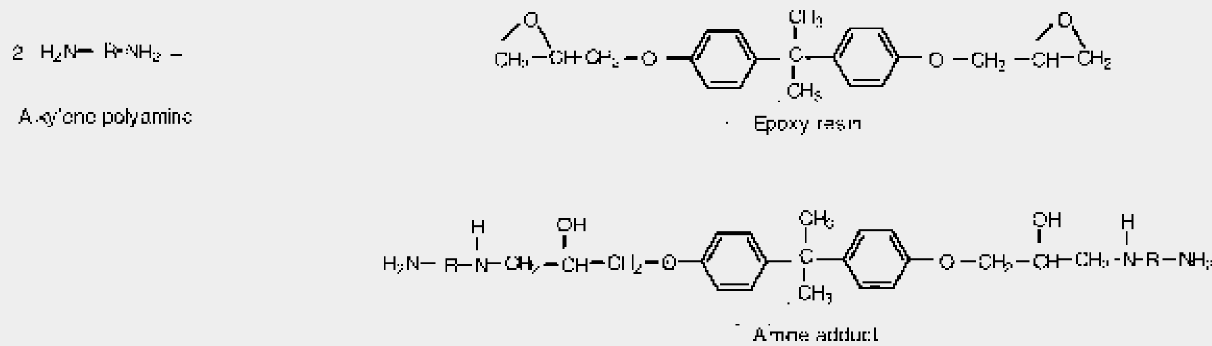
Reaction 2: Formation of carbamates by amines and moist air.

Phenalkamines

Phenalkamine curing agents are derived from 3-(n-penta-8'-decenyl)phenol which is the major constituent of cashew nutshell oil. Using this constituent (*Figure* 1), several multifunctional phenalkamines have been developed for low temperature cure applications.[12] These curatives are usually darkly colored and depending upon molecular weight, highly viscous.

Mannich Bases

These curatives are prepared by reacting amines with phenol (or alkyl phenols)



Reaction 3: Formation of standard amine adduct.

and formaldehyde to form condensates, or Mannich bases as they are commonly known. The reaction to form a Mannich base is depicted in *Reaction* 4.

Although this reaction decreases the functionality of the amine, the presence of a hydroxyl functionality on the aromatic ring produces a substantial accelerating effect on the epoxy/amine reaction. Mannich bases cure rapidly at low temperature (35-45°F).[11] They have better compatibility with epoxy resins than unmodified alkylene amines and are more resistant to blush and water spotting. In certain cases, external phenolic accelerators such as nonyl phenol are added to further improve low temperature cure performance. The choice of phenol-type and amine dictate the film performance properties. In some cases, plasticizers are added to improve film flexibility but these plasticizers often reduce the coatings' chemical resistance.

PERFORMANCE SURVEY OF LOW TEMPERATURE CURATIVES

Experimental Section

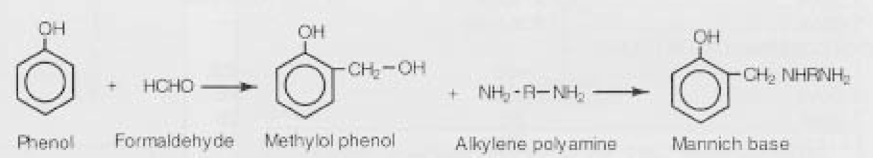
Several commercial curatives (Appendix I) were studied to determine the performance of these products in low temperature applications. A phenalkamine curing agent was used as the control in this study because its low temperature performance is well-known to the industry. Curative 1 is a modified amine adduct designed for low temperature applications. Curative 2 is an amine adduct supplied at 60% wt nonvolatiles in n-butanol/xylene. Low temperature epoxy coatings based on this curative have rapid hardness development and excellent solvent resistance. Curative 3 is a phenol-free, modified Mannich base that provides fast-setting, low temperature cure coatings. The physical properties of these curatives are shown in *Table* 1.

The first part of this coatings study evaluates the performance of these curatives with standard difunctional liquid epoxy resin (WPE = 198, Appendix I). Each binder system was mixed and reduced to Gardner H viscosity with an equal weight blend of MIBK/xylene/n-butanol. The varnish was mixed for five minutes and then applied to glass panels with a draw-down bar (1.5 mil DFT, 63 microns). After application, the coating was immediately placed in a constant temperature, constant humidity chamber. Film clarity, film tack, and pencil hardness were periodically evaluated over a two week period. Each binder system was cured using three different environmental conditions: 77°F, 55% relative humidity; 50°F, 90% relative humidity, and 40°F, 80% relative humidity. The results of this testing are summarized in *Table* 2.

In addition to determining the coating performance of clear films, we monitored the binder systems' cure rate using differential scanning calorimetry (DSC). This technique involves three steps. The first step is to run simultaneous DSC/TGA (thermogravimetric analysis) on the mixed components (no added solvent) to determine the temperature scanning range. This DSC/TGA technique shows the range of temperatures covered by the curing exotherm and sets the upper temperature limit where weight loss is still negligible (i.e., less than 1% wt).

After the temperature scanning range was established by the DSC/TGA run (from –50 to 170°F), a constant heating rate (10°C/min) DSC scan was performed to determine the total heat of reaction (ΔH_{total}) for each binder system. After reaching the upper temperature limit, the sample was quench-cooled to –50°C and reheated to determine if any post-curing occurred. In all cases, no post-curing was observed during the second DSC scan.

The final step of analysis was to load a freshly mixed sample into a DSC cell and immediately freeze the sample to –130°C (dry ice); while waiting for seven samples to be prepared. Total preparation time for these seven



Reaction 4: Mannich base reaction.

Table 1—Physical Properties of Curatives Used in this Study[a]

	Control (Phenalkamine)	Curative 1 (Amine Adduct)	Curative 2 (Amine Adduct Solution)	Curative 3 (Mannich Base)
Amine value	300-335	240-265	225-257	350-390
Viscosity, cP at 25°C	30,000	2500	2500	500
Gardner color	17 max	4 max	9 max	5 max
Solvent content, %w	0	0	40	0
Solvent	—	—	n-butanol/xylene	—

(a) See Appendix I for commercial names of these curatives.

samples was less than five minutes. The sealed DSC cells were stored in a refrigerator at 40°F for a predetermined number of days. On the appropriate day, one hermetically-sealed sample was removed from the refrigerator and immediately scanned by DSC using a 10°C/min temperature ramp. Integrating the area under this DSC scan gives the residual heat of reaction ($\Delta H_{residual}$) for the binder system after X days of cure at 40°F. The extent of reaction (or % cure) for each sample was calculated using equation (1).

$$\text{Extent of Reaction, \%} = (1 - \left(\frac{DH_{residual}}{DH_{total}}\right) * 100) \quad (1)$$

The results of the DSC study using standard liquid epoxy resin are summarized in *Figure* 2.

Table 2—Property Development with Liquid Epoxy Resin[a]

	Control (Phenalkamine)	Curative 1 (Amine Adduct)	Curative 2 (Amine Adduct Solution)	Curative 3 (Mannich Base)
Cure Conditions: 77°F and 55% relative humidity				
Solids content, %wt (theory)	81	85	65	88
Mix ratio, phr	72	60	124	40
Shyodu gel time (100 gm)	49 min	21 min	63 min	13 min
Set to touch, hrs.	0.5	1.25	1.25	0.75
Cotton free, hrs.	4.75	3.5	2.75	1.75
Thru-dry, hrs.	6.75	5.75	5.0	4.25
Days to clear film	1	1	1	1
Days to tack-free film	1	1	1	1
Pencil hardness (ASTM D3363)				
1 day	4B	F	B	HB
5 days	B	F	F	F
7 days	HB	F	F	F
14 days	F	H	F	F
Cure Conditions: 50°F and 90% relative humidity				
Days to clear film	14 (w/Sl.haze)	2	1	1
Film tack[b]				
1 day	Sl. tack	Tack-free	Sl. tack	Tack-free
3 days	Tack-free	—	Tack-free	—
5 days	—	—	—	—
Pencil hardness (ASTM D3363)				
1 day	6B	5B	6B	4B
5 days	5B	B	4B	HB
7 days	4B	B	B	F
14 days	3B	HB	HB	F
Cure Conditions: 40°F and 80% relative humidity				
Pot life @ 40°F (hrs to double initial viscosity)	2.5	2.5	3.0	2.5
Days to clear film	14 (w/haze)	3	1	5 (w/Sl. blush)
Film tack[b]				
1 day	M. tack	M. tack	Sl. tack	Sl. tack
3 days	Sl. tack	Tack-free	Tack-free	Tack-free
5 days	Tack-free	—	—	—
Pencil hardness (ASTM D3363)				
1 day	<6B	<6B	<6B	<6B
5 days	<6B	2B	<6B	HB
7 days	5B	2B	3B	F
14 days	3B	B	HB	F

(a) See Appendix I.
(b) Film tack: Sl=slight; M=moderate; V=very.

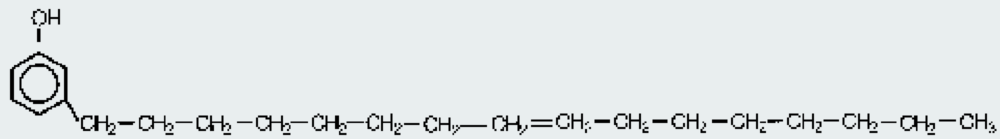


Figure 1—Chemical structure of 3-(n-penta-8'-decenyl)phenol.

Observations/Conclusions (with Standard Liquid Epoxy Resin)

Under standard ambient conditions (77°F and 55% relative humidity), we find that when each curative is combined with liquid epoxy resin, the coatings have relatively fast dry times with short gel times. Curative 3 has the highest reactivity because it has the fastest gel time and shortest Gardner dry times. Curative 2 has the longest gel time reading but this curing agent contains solvent that slows down the Shyodu gel time. Curative 2 is a solid resin in the absence of solvent, so a true measure of its gel time is impractical. The Gardner dry times for Curative 2 are the second fastest for the binders based on liquid epoxy resin but some of this speed may be a pseudo-lacquer dry from this amine adduct solution.

Acceptable pot life in fast-reacting epoxy/amine systems is a practical concern for coatings applicators. To better understand relative reactivities of these curatives in solvent-based coatings, the clear varnish formulations (reduced to Gardner H viscosity) were cooled to 40°F in an ice/water bath. Initial Brookfield viscosities ranged from 1200 cP - 1500 cP. At 40°F, each binder system required 2.5-3.0 hours for the varnish to double its viscosity.

At 50°F and 90% relative humidity, differences in tack-free times and clarity development start to become apparent. The film hardness development for Curative 3 is superior to the other curatives tested in this study. Curative 1 gives tack-free films overnight with good ultimate film hardness but the film clarity is slowed by the very high humidity level. The phenalkamine control has a longer tack-free time and, even after 14 days, is softer and hazier than the other curatives examined in this study.

At 40°F and 80% relative humidity, each curative has its own particular strengths and limitations which might influence selection of one curative versus another depending on the requirements of each application. In clear formulations, ultimate film clarity and blush resistance are very important properties but in pigmented formulations, other properties such as film hardness and tack-free times may be more important. To address these types of situations, a powerful graphing technique called a “spider chart” or a “radar chart” is available in today’s spreadsheet software packages.[13] The axes in spider charts are oriented so that better performance gives a longer ray; therefore, binders with more balanced performance have a larger area enclosed by their “performagon.” The performance of these curatives at 40°F is summarized in *Figure* 3.

The DSC technique used in this study is a powerful tool for evaluating the extent of reaction in low temperature cure binders. When cured with liquid epoxy resin, each of the curatives gives superior cure development at 40°F. To illustrate this fact, compare the low temperature reactivity of these curatives to the performance of polyamides. The cure rate of three polyamide curatives (accelerated and non-accelerated) was determined at 40°F using a similar DSC technique.[14] The results for the polyamides show that the extent of reaction on the third day ranged from 33-43% and even after 14 days cure, the extent of reaction was only 55-65%. With the low temperature curatives (*Figure* 2), the extent of reaction after three days ranged from 65-75% and after 14 days, the extent of reaction ranged from 75-95%.

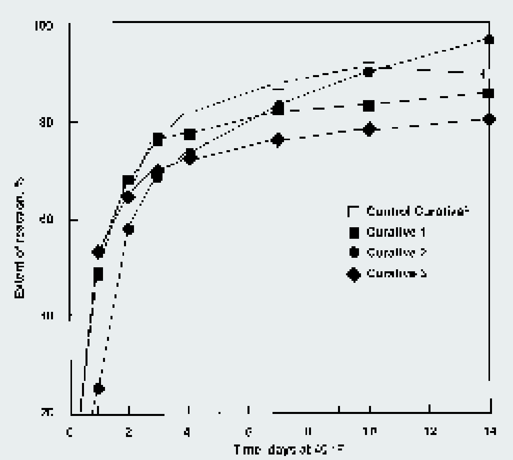


Figure 2—Cure development with liquid epoxy resins at 40°F.

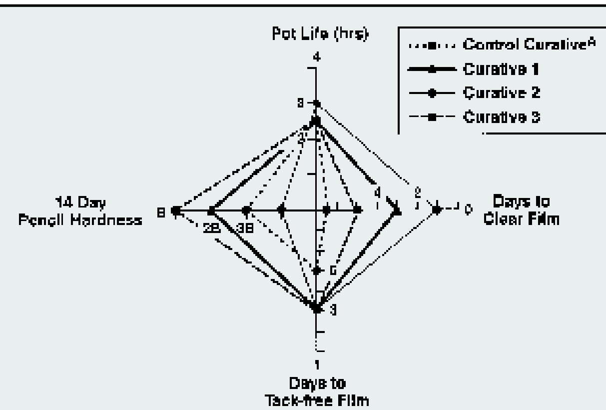


Figure 3—Performance of low temperature curatives (with liquid epoxy resin) at 40°F and 80% relative humidity.

Table 3—Physical Properties of Polyacrylated Epoxy Resin[a]

	Polyacrylated Epoxy One	Polyacrylated Epoxy Two	Polyacrylated Epoxy Three	Polyacrylated Epoxy Four
Viscosity, cP at 25°C	2180	950	700	110
Shyodu gel time (w/EPI-Cure® 3271)	7 min.	1 min.	5 min.	5.5 min.
Equivalent wt. by reaction with amine	177	140	192	150
WPE	210	310	220	315

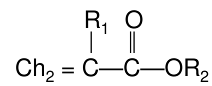
(a) See Appendix 1.

At 40°F, compared to the other curatives in this study, curative 2 has the slowest cure rate during the first four days, but it ultimately reaches the highest extent of reaction after 14 days. The superior reactivity of these new curatives, compared to polyamides, is most evident in the initial stages of cure when development of coating properties is most critical. For this reason, water spot resistance and early chemical resistance are expected to be much improved for the low temperature curatives.

While the curatives in this study possess excellent low temperature reactivity, other performance tests[15] indicate that each curative is best-suited for particular applications. Curative 1 is suitable for waste water applications and solvent-free marine coatings because it possesses superior water resistance and good corrosion resistance. Curative 2 is suitable for 2.8 pounds/gallon VOC-compliant formulations for industrial maintenance, marine and solvent-resistant tank linings. The high reactivity of curative 3, combined with its superior chemical resistance, makes it a candidate for tank linings, synthetic flooring and as a co-curing agent for polyamide-based coatings.

IMPROVED BINDER SYSTEMS FOR LOW TEMPERATURE CURE

Although these curatives have good performance with standard liquid epoxy resin, even under low temperature, high humidity conditions, an improved binder system can be formulated by replacing the liquid epoxy resin with a low viscosity epoxy/polyacrylate resin. These resins are based on standard Bis A epoxy resin that has been modified with multi-functional acrylate esters.[16] By tailoring the amount and type of modification, a wide range of resin reactivities can be obtained in the final binder (*Table* 3). Acrylate esters are represented by the general formula:



R_1 = H or CH3; R_2 = H or alkyl

The nature of the R groups determine the properties of each monomeric ester and the polymers derived from it. Aliphatic primary amines add rapidly across the acrylate double bond in a Michael's addition reaction. Secondary amines do not react well with the acrylic modifications. Aliphatic amines and cycloaliphatic amines are recommended for use with polyacrylated epoxy resins but amidoamines and polyamides generally do not work as hardeners for these resins.[17]

In the second phase of this study, we examined the performance of polyacrylate epoxy four with the low temperature curatives studied earlier. Using the testing procedures described in the Experimental Section, we applied the binder varnishes to glass panels and cured them in the environmental chamber. The results of this testing are summarized in *Table* 4.

Observations/Conclusions (With Polyacrylated Epoxy Resin)

Polyacrylated epoxy resins, in combination with curatives 1, 2, and 3, show significant advantages over

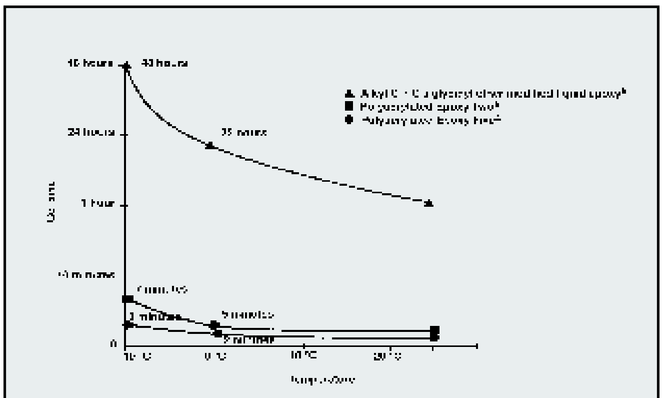


Figure 4—Polyacrylated epoxy-amine reactivity versus temperature.

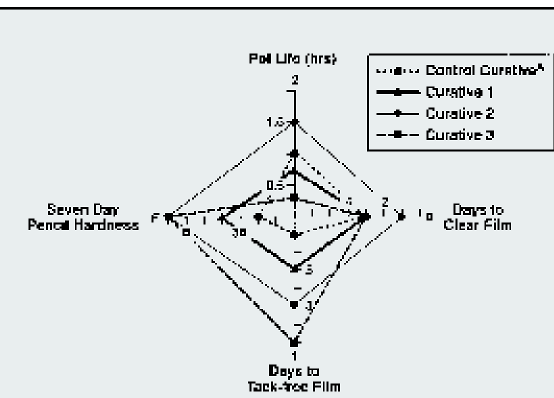


Figure 5—Performance of low temperature curatives with polyacrylated epoxy four at 40°F and 80% relative humidity.

Table 4—Film Properties with Polyacrylate-Modified Liquid Epoxy Resin[a]

	Control (Phenalkamine)	Curative 1 (Amine Adduct)	Curative 2 (Amine Adduct Solution)	Curative 3 (Mannich Base)
Cure Conditions: 77°F and 55% relative humidity				
Solids content, %wt (theory)	85	95	67	100
Mix ratio, phr	90	76	155	51
Shyodu gel time (100 gm)	43 min	18.5 min	27 min	5 min
Set to touch, hrs.	1.25	1.25	1.25	0.5
Cotton free, hrs.	3.5	4.0	3.5	1.25
Thru-dry, hrs.	13.5	6.0	5.25	1.75
Days to clear film	1	1	1	1
Days to tack-free film	4	2	1	1
Pencil hardness (ASTM D3363)				
1 day	<6B	4B	F	HB
5 days	5B	2B	F	F
7 days	4B	HB	F	F
14 days	2B	F	F	F
Cure Conditions: 50°F and 90% relative humidity				
Days to clear film	3	1	1	1
Film tack[b]				
1 day	Tacky	M. Tacky	Tack-free	Tack-free
3 days	M. Tacky	Tack-free	—	—
5 days	Tack-free	—	—	—
Pencil hardness (ASTM D3363)				
1 day	<6B	<6B	4B	B
5 days	5B	6B	HB	HB
7 days	3B	HB	F	F
14 days	HB	HB	F	F
Cure Conditions: 40°F and 80% relative humidity				
Pot life @ 40°F (hrs to double initial viscosity)	1.0	0.75	1.5	0.25
Days to clear film	3	3	1	3 days with Sl. haze
Film tack[b]				
1 day	V. tacky	Tacky	Sl. tacky	Tack-free
3 days	Tacky	Sl. tacky	Tack-free	—
5 days	Sl. tacky	Tack-free	—	—
7 days	Tack-free	—	—	—
Pencil hardness (ASTM D3363)				
1 day	<6B	<6B	<6B	<6B
5 days	<6B	5B	F	HB
7 days	<6B	4B	F	F
14 days	4B	2B	F	F

(a) See Appendix I.
(b) Film tack: Sl=slight; M=moderate; V=very.

standard liquid epoxies in low temperature, high humidity conditions. The improvements in blush resistance, clarity, and hardness development come from the rapidity of the Michael's addition reaction. A unique feature of epoxy polyacrylates is that their reactivity is relatively independent of temperature effects (see *Figure* 4).[17]

The advantage of this unique reactivity in low temperature applications is that the cure rate of polyacrylated epoxy resin is less affected by temperature than the cure rate of standard liquid epoxy resins. Polyacrylated epoxy resins bring two additional advantages to low temperature coating applications: increased blush resistance at high humidity and low viscosity for high solids or solventless formulations.

Table 5 shows that the gel times for these new binder systems are very short (i.e., less than 30 min). Curatives 2 and 3, when combined with polyacrylated epoxy four, have gel times that are two times faster than their gel times with standard liquid epoxy resin (*Table* 2). The control and curative 1 also have shorter gel times, but the difference is not as dramatic (e.g., curative 1/polyacrylate epoxy: 18 min gel; curative 1/standard epoxy: 21 min gel time).

Higher reactivity is also reflected in faster thin film dry times for room temperature applications. Curative 3 is particularly interesting because its thru-dry time decreases from 4.25 hr with standard liquid epoxy down to only 1.75 hr with polyacrylated epoxy four. Faster dry times are the key reason that polyacrylated epoxy resins are used extensively in flooring and adhesive applications. Other potential applications for fast dry epoxy resin systems include auto refinish, railcar applications, and industrial finish coatings.

Even at 40°F, the pot life of these polyacrylate epoxy system are too short for standard application equip-

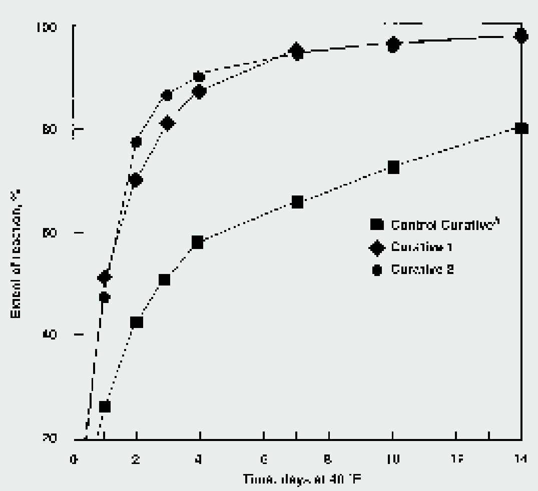


Figure 6—Cure development with polyacrylated epoxy four at 40°F.

ment. However, the low viscosity of these systems is perfectly suited for plural component, solventless equipment which is gaining acceptance in many shop-based applications.[18] Since the binder viscosity is low, heated plural component equipment may not be required to reach acceptable application viscosities.

Three formulation alternatives for longer pot life are to either (1) blend standard epoxy resin with the polyacrylated resin to decrease reactivity; (2) choose a lower reactivity modified resin such as polyacrylated epoxy three; or (3) select an aliphatic amine which is less reactive than the curatives tested in this study. The binder system based on curative 2 with polyacrylated epoxy resin four is unique because it has a pot life of 1.5 hours at 40°F with fast clarity and hardness development. The performance of each binder system at 40°F is summarized in *Figure* 5.

The long tack free times and slow hardness development in the Control suggest that it may not be suitable for use with polyacrylate epoxy four. Since polyacrylated epoxy four has a high level of modification, an alternative polyacrylated epoxy resin with lower modification (such as polyacrylated epoxy three) might be a more suitable epoxy resin for this curative.

In addition to testing the coating performance of these new binders, we determined their cure rates using the DSC technique described earlier. Curative 3 was not able to be included in this part of the study because the reactivity of the binder at 40°F was too fast to allow accurate determination of the ΔH_{total}. As soon as the two reactants were combined, a significant exotherm was observed—even when using precooled (40°F) epoxy resin and curative components. The results of this DSC study are summarized in *Figure* 6. The DSC results show that binders based on curatives 1 and 2 reach a high extent of reaction (>80%) after only three days cure. The control curative has a much slower reaction rate at 40°F. It eventually reaches a reasonable degree of crosslinking, comparable to polyamides, but the film hardness remains very soft (4B after 14 days).

SUMMARY

This paper summarizes recent efforts to evaluate epoxy/amine binder systems for low temperature cure coatings. The first section reviews the curing agent technologies used for these applications. Several commercially-available low temperature curatives were evaluated with standard liquid epoxy resin in clear varnish formulations to determine their film performance under different cure conditions: 77°F and 50% relative humidity, 50°F and 90% relative humidity, 40°F and 80% relative humidity A differential scanning calorimetry (DSC) technique is discussed in detail which measures the extent of reaction during the critical early cure period. Polyacrylate-modified liquid epoxy resins have been used for several years in the flooring industry for their superior low temperature reactivity. This study evaluates the performance of a polyacrylate-modified liquid epoxy resin with low temperature curatives.

The results of this study demonstrate that these new binder systems have significantly better clarity, blush-resistance, and hardness development than comparable systems based on standard liquid epoxy resin. Based on the positive results from this study, we have started testing the performance of these binder systems in white enamel starting point formulations.

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CARL SMITH joined Shell Chemical Company in 1980 as a member of Westhollow Technology Center's Analytical Department. Mr. Smith worked in the chromatography section supporting resins activities. Several years later, he transferred to Bellaire Technology Center where he worked in the Analytical Department and then the Petrophysical Services, both in support of Shell Oil Company's Exploration and Production activities. In 1993, he transferred to his current position in the Resins' Coatings Group at the Westhollow Technology Center. Mr. Smith specializes in the application and testing of starting point formulations based on waterborne and high solids epoxy binder systems.

References

(1) King, J.J. and Bell, J.P., *Epoxy Resin Chemistry*, Bauer, R.S., (Ed.), ACS Symposium Series 114, American Chemical Society, Washington, D.C., Chapter 16, 1979.

(2) Gough and Smith, "Accelerated Amine Curing of Epoxy Resins," *J. Oil & Colour Chemists Assoc.*, 43, 409-410 (1960).

(3) Zumstein, "Rapidly Hardenable Mixtures of Epoxy Resins and Polyamide Resins," US.S. 2,977,332.

(4) Lee and Neville, *Handbook of Epoxy Resins*, McGraw Hill Book Company, New York, 10-4, 1967.

(5) Hare, C.H., (Ed*.), Protective Coatings—Fundamentals of Chemistry and Composition*, Technology Publishing Company, 215, 1994.

(6) 2,4,6-(dimethylaminomethyl) phenol = EPI-Cure® 3253 (Shell Chemical Company); DMP-30 (Rohm and Haas); Ancamine® K54 (Air Products Pacific Anchor Chemicals)

(7) Tess, R.W., *Epoxy Resins—Chemistry and Technology*, May, C.A. (Ed.), Marcel Dekker, Inc., New York and Basel, 743-744, 1988.

(8) Lee and Neville, *Handbook of Epoxy Resins*, McGraw Hill Book Company, New York, 7-15 to 7-19, 1967.

(9) Mika, T.F. and Bauer, R.S, *Epoxy Resins—Chemistry and Technology*, May, C.A. (Ed.), Marcel Dekker, Inc., New York and Basel, 468, 1988.

(10) Ashcroft, W.R., *Chemistry and Technology of Epoxy Resins*, Ellis, B. (Ed.), Blackie Academic & Professional, London, 39 & 43, 1993.

(11) Ashcroft, W.R., in*Chemistry and Technology of Epoxy Resins*, Ellis, B. (Ed.), Blackie Academic & Professional, London, 53, 1993.

(12) Sielski, K., "Surfactants and Additives Derived from Cashew Nutshell Liquid," presented at Chemspec Europe, Amsterdam, March, 1991.

(13) "Radar Chart" is a chart-type found in Microsoft® Excel for Windows on the PC platform; supplied by the Microsoft Corp., "Spider Chart" is a chart-type found in DeltaGraph Pro 3 for the Macintosh platform; supplied by DeltaPoint, Inc.

(14) Thomas, R.W. and Lucas, P.A., "Development in Raw Materials for Epoxy-based Secondary Containment Systems" *Mod. Paint Coat.*, 108-116 (October 1994).

(15) Performance results published in Shell technical bulletins for EPI-Cure® 3378, 3292-FX-60 and 3251 Curing Agents. Unpublished results of white enamel formulations based on these low temperature curatives.

(16) McWhorter, M.F., U.S. Patent #4,051,195 to Celanese Polymer Specialties.

(17) Kincaid, D.S., "Epoxy Polyacrylate Hybrids - A Continuing Study," presented at the Epoxy Resin Formulator Division of The Society of the Plastics Industry, Inc., San Antonio, TX, March 9-10, 1992.

(18) Weinmann, D.J., "Solventless Epoxy Coatings for the Rail Car Industry," *Materials Performance*, 33, No. 6, 29-32 (June 1994).

Appendix I: Commercial Products Used in this Study

Generic Description	Trade Name	Supplier
Phenalkamine Curative (Control)	Cardolite® NC541	Cardolite Corporation
Modified Amine Adduct (Curative 1)	EPI-Cure® 3378 Curing Agent	Shell Chemical Company
Amine Adduct Solution (Curative 2)	EPI-Cure 3292-FX-60 Curing Agent	Shell Chemical Company
Mannich Base (Curative 3)	EPI-Cure 3378	Shell Chemical Company
Liquid Epoxy Resin	Epon® Resin 828	Shell Chemical Company
Polyacrylated Epoxy One	Epon Resin 8161	Shell Chemical Company
Polyacrylated Epoxy Two	Epon Resin 8111	Shell Chemical Company
Polyacrylated Epoxy Three	Epon Resin 8101	Shell Chemical Company
Polyacrylated Epoxy Four	Epon Resin 8021	Shell Chemical Company
Polyacrylated Epoxy Five	Epon Resin 8121	Shell Chemical Company
Alkyl C12-C14 glycidyl ether modified standard epoxy resins	Epon Resin 8132	Shell Chemical Company