Tert-Butyl Acetate: Non-HAP Solvent for High-Solids Epoxy Formulations

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Xylene is the traditional diluent solvent for formulating epoxy/amine paints used in protective coatings and linings. Currently, it is under regulatory pressure because it is on the hazardous air pollutant (HAP) list and it is also a volatile organic compound (VOC). Ketones and acetate esters are powerful solvents, but their use is limited by their reaction with the amine curatives before paint application. Tert-butyl acetate (t-BAc) proposed as a VOC-exempt solvent, is a nonreactive, non-HAP solvent suitable for both the epoxy resin and amine curative sides of a two-component epoxy system. Molecular modeling predicts very low reactivity of the t-BAc ester functionality with amine nucleophiles as a result of steric hindrance. Long-term aging studies with amine curatives in t-BAc solutions confirm these theoretical results. Kinetics of the reaction of amines with t-BAc and its n-butyl acetate isomer support the view that steric hindrance plays a major role in amine solution stability.

INTRODUCTION

The primary reason for reformulating a solvent system is to comply with hazardous air pollutant (HAP) and volatile organic compound (VOC) content limits. Whether dealing with old or new formulations, formulators should use non-HAP solvents to insure compliance with future regulations and to lower the toxicity of the product. Currently, aromatics are commonly used in epoxy formulations because they do not react with amines. However, toluene, xylene, and ethylbenzene are both an HAP and VOC.

In two-pack epoxy coatings, amine functional curatives react with ketones and aldehydes to form imines or Schiff bases,[1,2] and with esters to yield amides.[3] When a typical ketone, aldehyde, or ester is used to solvate an amine curative, the amino group gets consumed and becomes unavailable for reaction with the epoxy.[4] For this reason acetone and methyl acetate, currently non-HAP and VOC-exempt solvents, are not widely used in the formulation of epoxies despite their excellent regulatory profile.[5] Other solvents such as methyl amyl ketone and n-butyl acetate, while non-HAP and compatible with epoxies, have similar reaction problems with the amines and are also not used in these systems.

Previous work in our laboratories has demonstrated that tertiary butyl acetate (t-BAc), unlike methyl acetate and its isomer n-butyl acetate, is significantly less reactive in the presence of amines. On the other hand, t-BAc is very similar to nBuAc in its solvency power and may be used as a diluent in epoxy systems. To determine the range of applicability of t-BAc as a solvent for the amine curative side of a 2K-epoxy system, we chose to evaluate high-solids, highly reactive amines and amidoamines as well as classic polyamides.

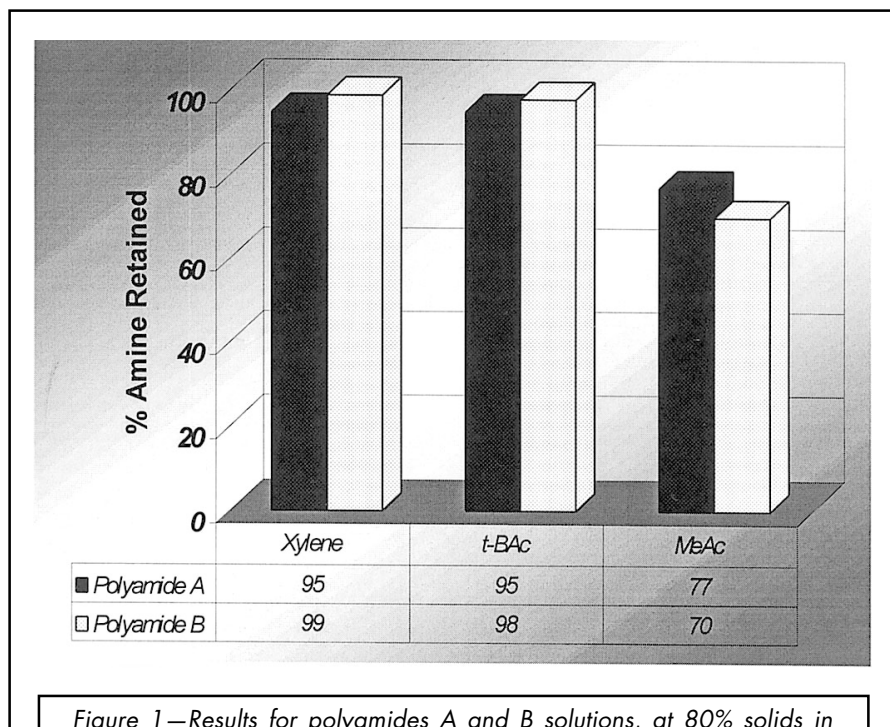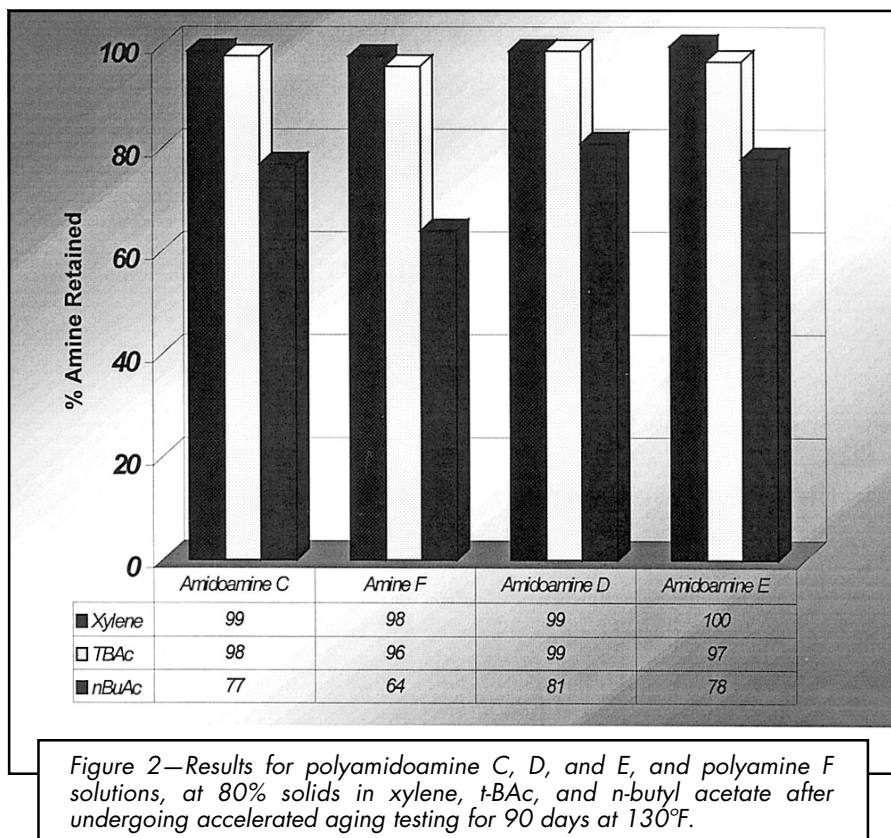|	Xylene	t-BAc	MeAc
■ Polyamide A	95	95	77
□ Polyamide B	99	98	70

Figure 1—Results for polyamides A and B solutions, at 80% solids in xylene, t-BAc, and methyl acetate after undergoing accelerated aging testing for 30 days at 140°F.

Figure 2—Results for polyamidoamine C, D, and E, and polyamine F solutions, at 80% solids in xylene, t-BAc, and n-butyl acetate after undergoing accelerated aging testing for 90 days at 130°F.

	Amidoamine C	Amine F	Amidoamine D	Amidoamine E
■ Xylene	99	98	99	100
□ TBAc	98	96	99	97
■ nBuAc	77	64	81	78

MATERIALS AND PROCEDURES

Materials

Epicure® 3115 and 3163 ("classic" poly-amides A and B) were obtained from Shell Corporation and used as supplied. Ancamide® 2353, 2386, 2396, (amido-amines C, D, E) and Ancamine® 2368 (high reactivity amines, amine F) were supplied by Air Products Inc. and were also used as supplied. Reagent grade quality of n-butyl acetate, methyl acetate, and xylene were used. T-Butyl acetate (TBAc™) and propylene glycol methyl ether (Arcosolv® PM) are products produced and supplied by Lyondell Chemical Company. Other solvents were purchased from Fisher Scientific.

Determining Storage Stability

Storage stability studies of the amine curatives were performed in different solvents (xylene, n-butyl acetate, me-thyl acetate, and t-butyl acetate). These were conducted by heating the prepared solutions in sealed glass bottles for 90 days at 50°C or 30 days at 60°C. Amine values were obtained before and after the accelerated aging using ASTM D2896.

Determination of Pseudo-First Order Kinetic Rates

Solutions of the amine-solvent com-binations were prepared to ensure pseudo-first order conditions. For each solution the response factors, as mea-sured by changes in height of infrared absorbance peaks, were determined to be linear at the expected concentration range (0.1 N – 0.025 N). The change in concentration with time was measured using 0.1 mm pathlength sealed IR cells and a Nicolet Nexus 670 FTIR spectrom-eter. Each reaction was monitored for 2.5 half-lives at three temperatures (40, 60, and 80°C) and each reading repre-sented 32 scans at 4 cm^{-1} resolution. The rates and activation energies were deter-mined by simple regression calculations.

Molecular Modeling

Each solvent was constructed using the drawing tools available in the Cam-bridge Soft Chem 3D software installed on an IBM 300 PL computer. The basic configuration for each molecule was se-lected from the minimized structure of methyl acetate. Then alterations to form the n-butyl and t-butyl esters and their corresponding amine adducts were made so the general molecular mor-phology was not changed. In this way energy differences resulting from vari-able conformations were minimized. Each structure was then minimized re-garding total MM2 molecular mechan-ics steric energy, and the change in steric energy in formation of the amine ad-duct was calculated by the difference in energy between the reactants and prod-ucts.

The density functional calculations were run by importing the Cartesian coordinates of the MM2 minimized structure into the input file format for the Schrodinger Corporation Jaguar 3.5 software. The density functional energy was calculated using the 631G** basis set with the Becke 3: LYP functional and were run on a Silicon Graphics Indigo2 work station using an R 8000 processor. All geometries were completely opti-mized, and the reaction energies again calculated by difference.

## RESULTS AND DISCUSSION

Storage Stability

Amine functional curatives for two-pack epoxy coatings are known to react with ketones and with esters to yield unreac-tive by-products. Previous work has demonstrated that tertiary butyl acetate, unlike other linear and simple acetates, is significantly less reactive in the pres-ence of nucleophiles. t-BAc was studied as a replacement solvent for the amine curative side in a 2K-epoxy system. In this study we evaluated high-solids, high reactivity cyclic amines and amido-amines as well as classic.

Accelerated aging of amine curative/ solvent blends was conducted using el-evated temperatures as indicated in the experimental section to simulate a one-year shelf life. Xylene was chosen as the standard inert solvent. t-BAc was used alone as a diluent and blended with pro-pylene glycol methyl ether as its co-sol-vent to adjust the polarity of the me-dium. Conversion of amine functional-ity to amide groups was determined by wet titration.

Table 1—MM2 Steric Energies (kcal/mole)

Reactants	Stretch	Bend	Non-Bonded	Total
t-BAc	0.691	3.497	2.937	7.445
nBuAc	0.449	1.689	4.674	6.812
IPA	0.109	0.245	0.687	1.131
Adducts				
t-BAc/IPA	1.238	11.326	6.321	19.588
nBuAc/IPA	0.844	6.010	4.813	12.255

Table 2—Steric Engergy Change: Amine/Ester Addition

$$R_1CO_2R_2 + (CH_3)_2(CHNH_2 \rightarrow R_1C(OH)[NHCH(CH_3)]R_2$$
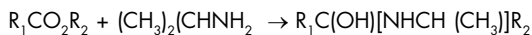
Ester	ΔE_s (kcal/mole)	Relative Rate (25°C)
tBAc	11.01	1.2×10^{-5}
nBuAc	4.31	[1.0]

Energy Difference: 6.70 kcal/mole

Relative Rate $= e^{-(E_1 - E_2)/RT}$

+ 4 - +7 kcal/mole

Figure 3—Difference in energy of activation between t-Bac and nBuAc in the presence of an amine nucleophile as derived from density functional theory molecular modelling.
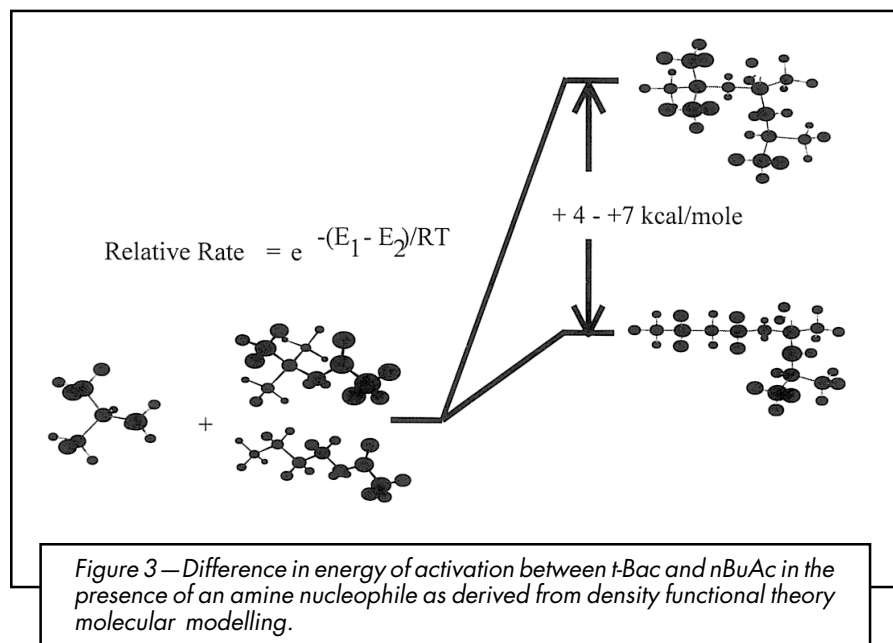
Figure 1 lists the amine values for two higher molecular weight amino-polyamide products at 80% solids. Within the experimental variability of the wet chemical test, there appears to be no difference between t-BAc and xylene. Some amine loss is noted even for xylene; this is attributed to oxidation or amine-amide reactions. The comparative example, methyl acetate, reacts quite extensively with the amines present in the samples.

Figure 2 lists the amine values from stability studies using higher amine content, higher solids, and lower molecular weight curatives. Once again, t-BAc and xylene have almost identical amine values after the test period. n-Butyl acetate, a structural isomer to t-BAc, demonstrates significant reaction with the curatives thus effectively lowering the functionality of the epoxy/amine coating system. Lowering the functionality of the amino curative is more problematic when lower molecular weight epoxy resins such as DGEBA are used since these are typically slow to cure.[6] Higher molecular weight epoxies provide faster drying and chemical resistance even before crosslinking is achieved; this "lacquer effect" does not occur with lower molecular weight epoxy resins.

Molecular Modeling

The lower reactivity of t-BAc compared to nBuAc can be accounted for, at least semiquantitatively, by calculating the energy required to form the ester-amine adduct. Two methods were used to study the two solvents: analysis of changes in steric strain by MM2 molecular mechanics and geometry optimized energies from density functional theory (DFT).

Although it is realized that molecular mechanics is not often used for modeling systems where bonds are broken or formed, only the relative reactivities will be extracted from the analysis. The general energy terms of the bonds, formed or broken, will be canceled, and the residual energy differences will represent changes in steric stability as the reaction proceeds. Furthermore, the reactions studied are single step additions to form a reactive intermediate. For this reason it is not necessary to fully model the transition state since the energy of the overall reaction should accurately mirror the corresponding changes in activation energy, and, hence, the kinetics.

The MM2 energy of each molecule was calculated using the Chem3D software package from CambridgeSoft Corporation. The amine chosen for the study was isopropyl amine and was selected since the structure around the amine nitrogen is not atypical of many amines used in product formulations. Full geometry optimization was performed on all molecules. The final MM2 energies are summarized in *Table* 1. Reaction energies are listed in *Table* 2. The results suggest that the formation of the t-BAc-IPA adduct requires over 6 kcal/mole more energy compared to the same adduct arising from nBuAc. This is sufficient, assuming identical Arrhenius preexponential factors, to explain a decrease in rate by 100,000 when t-BAc is substituted for nBuAc.

Finally, the two systems were examined using the energies from density functional theory. Full DFT geometry optimization was carried out on all molecules using the Jaguar 3.5 software available from Schrodinger, Inc.

A summary of the results depicted in *Figure* 3 further supports that the relative rate of reaction, when substituting the delta in activation energy required for the formation of the amine-ester intermediates, between the amine nucleophile and t-BAc should be much slower than with nBuAc. As the energy of activation increases the rate of the reaction

Table 3—Rates of Solvolysis Per Second for Amine Curatives at Three Different Temperatures

Amine	Solvent	Temperature (°C)			Extrapolated 25°
		40°	60°	80°	
Amidoamine C	t-BAc	$(1.16 \pm 0.04)E-08$	$(5.3 \pm 0.2)E-08$	$(7.5 \pm 0.2)E-08$	7.1E-09
	nBuAc	$(5.0 \pm 0.4)E-07$	$(7.6 \pm 0.4)E-07$	$(1.09 \pm 0.09)E-06$	3.6E-07
Amine F	t-BAc	$(7.0 \pm 0.2)E-09$	$(1.35 \pm 0.03)E-08$	$(2.86 \pm 0.02)E-08$	3.6E-09
	nBuAc	$(7.3 \pm 0.2)E-08$	$(1.0 \pm 0.4)E-07$	$(2.2 \pm 0.2)E-07$	4.2E-08

will decrease. This conclusion is based on the energy differences of the amine adducts alone and does not include consideration of any additional rate loss due to difficulty of the amine actually approaching the carbonyl of the ester. In

that case, t-BAc would be expected to prove even less reactive. It is, therefore, not surprising that experimental rate studies show that t-BAc behaves entirely as an unreactive solvent.

Pseudo-First Order Kinetic Rate Evaluations

Pseudo-first order rates were determined for nBuAc and t-BAc both in the presence of a cyclic amine and then a linear aminopolyamide. The time scans showed that, qualitatively, t-BAc reacts much more slowly than the nonbranched acetate. This is in agreement with the results ob-

tained from MM2 and DFT calculations for the model amine-solvent configurations. The steric hindrance provided by the t-butyl adduct appears to inhibit its reaction with the amino group of the curative. The data was then analyzed using common linear regression tools. The rates obtained for each solvent-amine combination are summarized in *Table* 3.

The results show that t-BAc is significantly slower to react with amine curatives than nBuAc. The calculated solvolysis rates were used to determine activation energies and differences for each of the curatives (see *Table* 4). A difference of a factor of 10 in the rate of solvolysis yielded activation energies between 4 and 7 kcal/mole for the corresponding solvents-amine products. This is in agreement with the theoretical activation energy calculation performed on the same solvents with isopropylamine.

Formulating

The stability tests performed with the same solvents and amine curatives demonstrate that the observed rate decrease is enough to slow down the amine side reaction by 32% in the case of the amine and 19% for the aminoamide. This is a significant saving when looking at the shelf-life of the coating. The negligible difference between amine content in xylene and t-BAc further supports its use in two-pack epoxy formulations. t-BAc also exhibits solvating properties similar to those of xylene, making this an easy substitution (*Figure* 4).

Table 4—Activation Energies for Amine Curatives

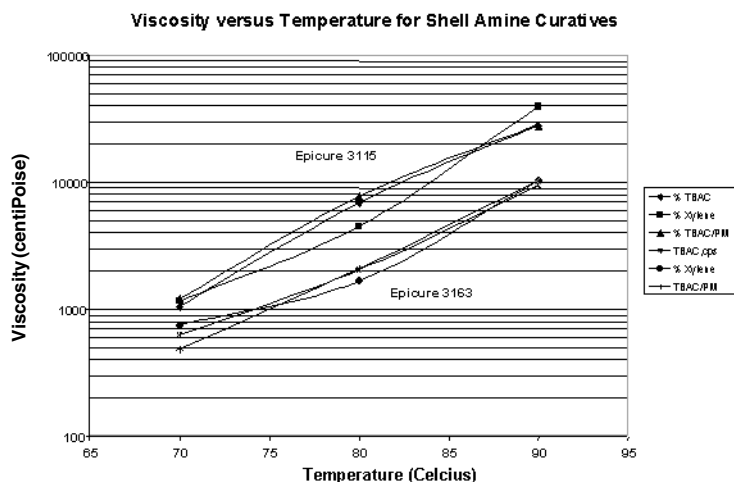| Solvent	Amine	E_{act} (kcal/mole)
t-BAc	Amidoamine C	4.91
	Amine F	7.76
nBuAc	Amidoamine C	4.27
	Amine F	5.95

Figure 4—Viscosity versus concentration comparison between xylene and t-BAc for two amine curatives.

Table 5—High Solids, Fast Dry White Enamel

| | Standard Formula Xylene | Parts by Weight | Reformulated with t-BAc | |
			Non-HAP	Non-VOC Non-HAP
Part A		**Part A**		
Epon 1001X75	500	Epon 1001X75	500	
TiO$_2$	307	TiO$_2$	307	
Xylene	112	t-BAc	55	
		Aromatic 100	10	
		Propylene glycol Methyl ether	47	
Beetle 216-8	3.54	Beetle 216-8	3.54	
Nuosperse 657	2.84	Nuosperse 657	2.84	
Part B		**Part B**		
Amidoamine	131	Amidoamine	131	
Xylene	30	t-BAc	30	
Volume ratio A/B	80/20	Volume ratio A/B	80/20	80/20
Wt% solids mixed	74.8	Wt% solids mixed	74.8	74.8
VOC lb/gal	2.74	VOC lb/gal	2.73	2.15
HAP lb/gal	2.74	HAP lb/gal	1.28	1.28

Table 6—Rapid Drying, Flexible Epoxy/Polyamide White Enamel

	Standard Formula Xylene	Parts by Weight	Reformulated with t-BAc	
			Non-HAP	Low-VOC Non-HAP
Part A		**Part A**		
Epon 1001X75	301	Epon 1001X75	301	
TiO_2	175	TiO_2	175	
Calcium carbonate	65	Calcium carbonate	65	
Barium sulfate	20	Barium sulfate	20	
Xylene	221	t-BAc	115	
		Aromatic 100	30	
		Propylene glycol Methyl ether	76	
MAK	15	MAK	15	
Beetle 216-8	12	Beetle 216-8	12	
Part B		**Part B**		
Polyamide	122	Polyamide	122	
Xylene	70	t-BAc	55	
		Aromatic 100	15	
Volume ratio A/B	75/25	Volume ratio A/B	75/25	75/25
Wt% solids mixed	61.6	Wt% solids mixed	61.6	61.6
VOC lb/gal	3.87	VOC lb/gal	3.76	2.79
HAP lb/gal	3.87	HAP lb/gal	0.84	0.84

Table 7—Performance Properties for a Two-Pack Epoxy Primer After Xylene Reformulation with an 80:20 t-BAc and Aromatic 100 Blend

	Standard Formulation with Xylene	Reformulated tBAc/Aromatic 100
Film properties after seven days air dry		
Thickness (mil)	1.93	1.94
Impact resistance F/R (lb/lb)	160/160	160/160
Crosshatch adhesion (%)	100	100
Mandrel bend	1/8 in. passed	1/8 in passed
ASTM B117 Salt Spray, 800 hr 1 hr mix time scribe creep (mm), blister rating	<1mm, 7VF	<1 mm, 7VF
ASTM B117 Salt Spray, 800 hr 24 mix time scribe creep (mm), blister rating	<1mm, 7VF	<1 mm, 7VF

formulation. This higher molecular weight epoxy resin gives substantially faster dry-to-touch times and higher flexibility resins at the expense of VOC content of the formulation.

Finally, we tested the performance of a two-pack epoxy primer formulation. When we perform the reformulation it is observed that the performance of the resulting films are clearly unaffected. These continue to display high performance properties as expected since the solvent does not adversely affect the amine curative (see *Table 7*).

SUMMARY

Tert-butyl acetate does not react appreciably with epoxy amine curatives and can replace substantial amounts of xylene and other aromatics in two-component epoxy-coating systems. When t-BAc is added to the list of VOC-exempt solvents, it will become an excellent tool to reduce the HAP and VOC content of such formulations. Unlike other esters, t-BAc does not react appreciably with the amine curatives even under extended storage conditions. In fact, t-BAc is almost as inert as xylene under the accelerated aging conditions recommended by manufacturers of epoxy resins. These observations are supported by theoretical calculations that suggest that the steric bulk of the tert-

Until the EPA publishes the final rule exempting t-BAc from VOC regulations, t-BAc only provides HAP-reduction benefits when replacing toluene or xylene. *Tables* 5 and 6 illustrate the HAP and VOC reduction benefits likely to occur when t-BAc is substituted for HAP-listed aromatics in 2K epoxy formulations. The VOC contents in the right column assume that t-BAc is VOC exempt.

When using t-BAc as a diluent/solvent for epoxy systems, the high volatility of the t-BAc can be an issue. Evaporation during spraying is always a concern for light solvents, especially those that are currently VOC exempt (acetone, methyl acetate). A common reformulation tool is to combine higher boiling solvents and low boiling solvents to mimic a standard control. With xylene chosen as the most common diluent, two

blends would work effectively in reformulated products as a direct replacement. An 80/20 mixture of t-BAc and Aromatic 100 or t-BAc and methyl amyl ketone have similar evaporation rates as xylene and provide a relatively good "tail" solvent. When t-BAc becomes VOC exempt, these combinations will maximize the VOC content reduction of the coating. The use of non-HAP glycol ether such as propylene glycol methyl ether in these formulations ensures a good solvency of the polar amines and epoxy adducts at the final stages of film drying and also moderates the high t-BAc evaporation rate.

For the formulations used in this paper, a commercial epoxy resin solution in xylene was chosen. Replacing the xylene with t-BAc would further reduce the HAP and VOC content of the final

butyl group inhibits the reaction with the amine. In practice, when formulating with t-BAc for sprayable applications, a slight amount of a heavier solvent is recommended to slow down the evaporation rate and improve flow and leveling. Suitable "tail" solvents include propylene glycol methyl ether and MAK. VOC and HAP compliance will soon be possible with solvent-based 2K epoxy systems as solvents such as t-BAc are developed and exempted.

AKNOWLEDGMENT

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