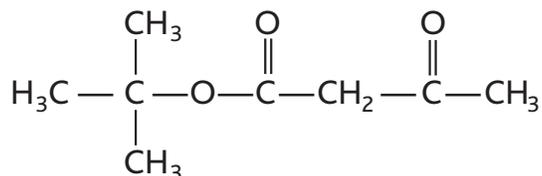


Eastman™ t-BAA (tertiary-butyl acetoacetate)

for the synthesis of acetoacetyl-functional resins



Eastman™ t-BAA

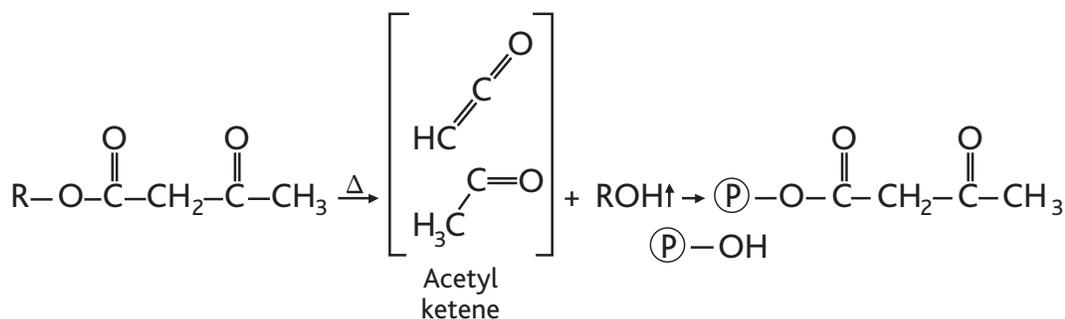
Introduction

Eastman™ t-BAA (tertiary-butyl acetoacetate) efficiently prepares acetoacetylated resins from a variety of hydroxyl-bearing polymers. The acetoacetyl functionality gives polymers the ability to undergo a variety of cross-linking reactions while adding desirable resin and finished coating properties.

The availability of Eastman™ AAEM (acetoacetoxyethyl methacrylate) provides resin producers with an easy method to incorporate acetoacetyl groups onto the backbone of acrylic resins. However, it is more difficult to add acetoacetyl groups to other resin types. This has been accomplished by transesterifying acetoacetic esters such

as Eastman™ MAA (methyl acetoacetate) or Eastman™ EAA (ethyl acetoacetate) with pendant or end-group hydroxyls on a polymer. In polyester resins, this method has the disadvantage of some ester interchange along the polymer backbone.

The acetoacetylation mechanism using t-BAA is distinctly different from that of typical transesterification reactions and allows for the acetoacetylation of polyesters without altering the backbone structure. Furthermore, this reaction is 15 to 20 times faster than reaction with MAA or EAA. t-BAA is equally effective in acetoacetylating primary and secondary hydroxyls.



Transacetoacetylation mechanism

Benefits of acetoacetyl chemistry in coatings

- **Reduced solution viscosity**

Adding the bulky acetoacetyl group to a polymer chain increases chain separation and decreases hydrogen bonding, thereby reducing resin solution viscosity.

- **Conventional cross-linking capabilities**

The acetoacetyl group reacts with conventional cross-linkers such as melamines and isocyanates.

- **Additional cross-linking capabilities**

Through mechanisms such as the Michael reaction and enamine formation, the acetoacetyl group offers innovative, ambient temperature cross-linking systems.

- **Improved adhesion to metals**

The ability of the acetoacetyl group to chelate metals provides excellent adhesion to and corrosion resistance on metallic substrates.

Acetoacetylation of polyester resins using Eastman™ t-BAA

The synthesis of acetoacetylated polyester resins using Eastman™ t-BAA is similar to a typical transesterification method. The acetoacetylation step is carried out at the end of the esterification process and can be done in the same equipment. A laboratory synthesis procedure for the preparation of an acetoacetylated polyester resin, starting with Eastman™ polyester formulation HS-3-1NCp, is given in Table 1.

Table 1 Eastman™ polyester formulation HS-3-1NCp

Component	Moles
Eastman NPG™ glycol	37.1
Trimethylolpropane (TMP)	1.6
Eastman™ 1,4-CHDA (1,4-cyclohexanedicarboxylic acid)	15.1
Phthalic anhydride (PA)	10.1
Molecular weight (M_n) = 675	
Calculated hydroxyl no. = 222	
Acid no. = 9 (mg KOH/g resin)	

Resin HS-3-1NCp was prepared using a standard fusion cook process as described in Eastman publication N-321. While acetoacetylation can be carried out in one additional step at the end of this synthesis, resin HS-3-1NCp was isolated neat so that incremental levels of acetoacetylation

could be evaluated. Using the following procedure, the resin was acetoacetylated to 20%, 40%, and 90% conversion of the available hydroxyls. The calculations for determining the amount of t-BAA to use for a specific conversion and the theoretical amount of t-butanol that should be evolved are also shown. Table 2 illustrates the effects of acetoacetylation on the solution viscosity and color of the polyester resin.

Acetoacetylation procedure

- Charge neat resin to four-neck round-bottom flask equipped with air-driven stirrer, thermocouple with temperature controller, nitrogen purge, steam-jacketed, packed partial condenser, Dean-Stark trap, and full condenser.
- Add synthesis solvent to desired solids content. Because of its relatively high boiling point, Eastman™ EEP is excellent as the acetoacetylation synthesis solvent. Raise temperature to 140°C.
- Add Eastman™ t-BAA to obtain the desired extent of acetoacetylation (see the following calculation).
- Allow reaction to proceed at 140°C until theoretical amount of tertiary-butanol (t-BuOH) distillate is achieved or until distillate evolution stops.
- Remove from heat and allow to cool.

Acetoacetylation calculation for polyester resin HS-3-1NCp

■ Amount of Eastman™ t-BAA:

$$\frac{\text{Resin wt}}{\text{Resin eq wt}} \times (\text{t-BAA eq wt}) \times \text{desired fraction of acetoacetylation}$$

Resin equivalent weight = 253

t-BAA equivalent weight = 158

For a 20% acetoacetylation of 1,000 g of resin HS-3-1NCp:

$$\text{t-BAA weight} = (1,000/253) \times 158 \times 0.2 = 125.0 \text{ g t-BAA}$$

■ Theoretical t-BuOH distillate:

$$\text{Distillate weight} = \frac{\text{wt t-BAA}}{\text{t-BAA eq wt}} \times (\text{t-BuOH eq wt})$$

t-BuOH equivalent weight = 74

$$\begin{aligned} \text{Theoretical t-BuOH distillate} &= (125.0/158) \\ &\times 74 = 58.5 \text{ g t-BuOH} \end{aligned}$$

The viscosity data given in Table 2 and shown graphically in Figure 1 clearly demonstrate the reduction in solution viscosity that can be obtained through acetoacetylation. For most resin systems, the largest reduction in solution viscosity occurs in the first 10%–40% of acetoacetylation. At high levels of acetoacetylation, some color is imparted to the resin.

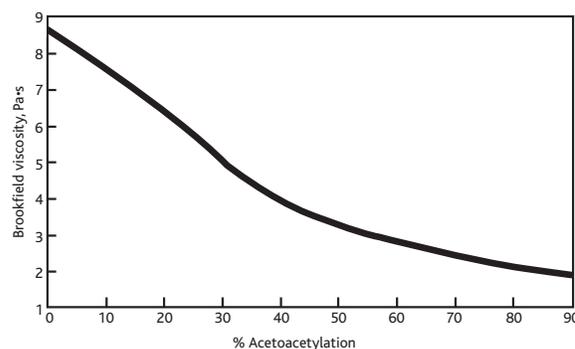
Table 2 Viscosity and color of acetoacetylated resin HS-3-1NCp

% Acetoacetylation	0	20	40	90
Determined wt% solids ^{a,b}	79.1	80.7	80.9	80.7
Brookfield™ viscosity, mPa·s	8,640	6,540	3,820	1,810
Gardner™ viscosity	Z ₄ –Z ₅	Z ₄	Z ₂	Y
Gardner™ color	<1	<1	<1	2

^aIn Eastman™ EEP

^b30-minute exposure at 163°C (325°F)

Figure 1 Effect of acetoacetylation on resin solution viscosity



Melamine cross-linked enamels and properties

To examine the effect of acetoacetylation on a finished coating, a series of enamels were prepared from the resins in Table 2 using the enamel formulation shown in Table 3. The data in Table 4 indicate that, at similar viscosities, there is a consistent reduction in the determined volatile organic compound (VOC) content of the coatings at increasing levels of acetoacetylation.

Table 3 Enamel formulation

Component	Grams
Resin solution @ 80 wt% solids in Eastman™ EEP	239.0
Cymel™ ^a 303 melamine resin	60.0
Ti-Pure™ ^b R-900 TiO ₂	165.0
pTSA catalyst @ 40% solids in isopropyl alcohol	1.5
Fluorad™ ^c FC-430 flow control agent @ 20 wt% solids in Eastman EEP	2.5
Solvent blend ^d	As needed to adjust viscosity

^aCytec

^bDuPont

^c3M

^dSolvent blend—Eastman™ MAK/ Eastman™ EEP/ n-butyl alcohol (70/15/15)

Table 4 Enamel viscosity and VOC^a

Resin % acetoacetylation	0	20	40	90
Viscosity, #4 Ford cup, s	41	40	40	41
Determined VOC, ^b g/L (lb/gal)	307 (2.56)	286 (2.39)	270 (2.25)	238 (1.99)

^aResin/cross-linker ratio = 75/25; Pigment/binder ratio = 40/60

^bEPA Method 24: 90-minute film exposure at 110°C (230°F)

Effect of acetoacetylation on cured film properties

The MEK resistance of the cured films shown in Table 5 demonstrates that measurable cross-linking has been obtained at each level of acetoacetylation. The improvements in impact resistance observed here without a sacrifice in hardness are consistent with data obtained

in other Eastman studies and by other people. The ability of the acetoacetyl group to chelate metallic substrates has consistently given improved adhesion, which results in better salt-spray resistance.

Table 5 Cured film properties^a

Resin % acetoacetylation	0	20	40	90
Average film thickness				
μm	38–51	38–51	38–51	38–51
Mil	1.5–2.0	1.5–2.0	1.5–2.0	1.5–2.0
MEK double-rub resistance	200+	200+	200+	200+
Pencil hardness, mar	H	H	H	H
Tukon hardness, knoops	18.73	18.91	18.16	15.21
Impact resistance, forward/reverse				
N-m	3.6/1.4	14.9/10.4	9.5/4.5	15.4/9.9
in.-lb	32/12	132/92	84/40	136/88
Salt spray after 1,000 h, creepage				
mm	3.175	<1.588	<1.588	<1.588
in.	0.125	<0.0625	<0.0625	<0.0625
Cleveland™ humidity after 100 h, ^b				
% gloss retention	99	97	100	98

^aEnamels applied to steel substrates and cured 30 min at 163°C (325°F)

^bNo blistering observed on any of the coatings

Acetoacetylation of other classes of resins

Although this publication deals with the acetoacetylation of polyester resins, the utility of the procedure is not limited to polyesters. Most resins with pendant hydroxyl

groups, such as cellulosics, acrylics, and epoxies, can be acetoacetylated using Eastman™ t-BAA.

Synthesis tips

Resin design

The design of the resin to be acetoacetylated will depend on the intended use of the acetoacetyl groups. For example, if the acetoacetyl groups are to be used for viscosity reduction, the resin should be designed to have a hydroxyl number of 150 or more and an acid number of 2 (mg KOH/g resin) or less. Higher acid numbers can lead to continuation

of the esterification during the acetoacetylation reaction. This increase in molecular weight has been observed to offset some or all of the viscosity reduction typically provided by the acetoacetyl groups.

Table 6 lists suggested resin characteristics and extent of acetoacetylation for various desired properties.

Table 6 Resin design to achieve desired properties with acetoacetylation

Desired property	Resin OH no. (mg KOH/g resin)	Resin acid no. (mg KOH/g resin)	% Conversion to acetoacetate
Viscosity reduction	150+	<2	40–90
Conventional cross-linking	100+	N.A.	60–90
Alternative cross-linking	100+	N.A.	60–90
Adhesion to metal	N.A.	N.A.	10–50

Addition of Eastman™ t-BAA

The easiest procedure for the acetoacetylation of a coating resin involves adding t-BAA as the last stage of the synthesis. The resin should be cooled to acetoacetylation temperature (see the following) prior to addition.

Acetoacetylation temperature

The optimum temperature for acetoacetylation reaction is between 120°C and 160°C. The reaction can be carried out below 120°C, but the speed of the reaction will be reduced. Similarly, the reaction can be carried out above 160°C, but there will be some risk of yellow color formation.

Synthesis solvents

A synthesis solvent should be used for the acetoacetylation reaction only if it is necessary to achieve thorough mixing

of the Eastman™ t-BAA with the resin. Resins that are low in viscosity at the desired acetoacetylation temperature usually will not require a synthesis solvent. Higher-viscosity resins may require the use of a synthesis solvent to allow both thorough mixing of the t-BAA and efficient evolution of the t-butanol distillate. The synthesis solvent should be chosen based on these criteria:

- Boiling point of the solvent at or above the desired acetoacetylation temperature.
- No hydroxyls on the solvent molecule.
- Low water content of the solvent.

Aromatic hydrocarbons, glycol ether esters, and Eastman™ EEP have been used successfully.

Reaction progress

One method for following the progress of the acetoacetylation reaction is to monitor the t-butanol distillate evolved. Nuclear magnetic resonance (NMR) and high-pressure liquid chromatography (HPLC) studies using lab-scale (3- to 5-liter) reactions have indicated that the acetoacetylation reaction is generally complete within the first 15–45 minutes (see Table 7). Evolution of the t-butanol distillate typically requires an additional 1.5 to 2.5 hours.

This method can be misleading, however. A small amount of t-butanol usually remains in the resin after completion, so that the actual distillate evolved is less than the theoretical distillate. In some cases, the problem may be overcome by using a small amount of azeotropic solvent such as heptane or cyclohexane. Also, the freezing point of t-butanol is 25°C. The t-butanol can solidify in condenser

columns, which may further reduce the amount of distillate measured.

It should be noted as well that the rate of the acetoacetylation reaction with Eastman™ t-BAA does not depend on the removal of t-butanol. It is necessary to remove the distillate to drive the reaction to completion. In some coatings, the t-butanol could be left in the resin, where it may serve to stabilize melamine cross-linkers. A more accurate determination of reaction completion can be made with HPLC. Tables 7 and 8 show the correlation of HPLC with NMR analysis, and the HPLC conditions for detecting t-BAA, respectively. For more information on Eastman starting point formulation HS-3-6T, see Eastman publication N-362.

Table 7 HPLC and NMR results correlation
Resin HS-3-6T

Target % acetoacetylation = 90
Calculated initial wt% Eastman™ t-BAA = 27.3
Determined (HPLC) initial wt% t-BAA = 29.63

Sample no.	Time (min)	HPLC wt% t-BAA	HPLC % t-BAA reacted	NMR % t-BAA reacted
1	5	10.884	63.3	61.4
2	10	3.382	88.6	90.5
3	15	2.121	92.8	93.5
4	20	2.337	92.1	94.2
5	25	1.483	95.0	94.4
6	45	1.647	94.4	95.9
7	60	1.372	95.4	—
8	75	0.738	97.5	—

Table 8 Chromatographic conditions

Mode	Reverse phase
Column	Hypersil™ ODS, 4.6 × 100 mm, 5-micron particles
Column temp	35°C
Gradient	(solvent A = CH ₃ CN; solvent B = 0.005 M tetrabutylammonium phosphate, TBAP)
Step 1	10% A to 90% A, 4 minutes, linear
2	90% A, hold for 2 minutes
3	90% A to 10% A, 2 minutes, linear
Equilibration	10% A for 4 minutes
Injection volume	5 microliters
Detection	UV @ 210 nm

Summary

Eastman™ t-BAA (tertiary-butyl acetoacetate) provides an efficient technique to acetoacetylate hydroxyl-bearing polymers. Acetoacetylation of coatings resins is effective for the production of lower-viscosity resins, which allow for formulation of higher-solids coatings. These coatings are important for achieving VOC compliance. In addition to its influence in reducing solution viscosity, the acetoacetyl group cross-links with melamine, giving improved impact and salt-spray resistance. For more information about acetoacetyl chemistry in thermoset coatings, ask for Eastman publication N-322—*Utility of Eastman™ AAEM (acetoacetoxyethyl methacrylate) in thermoset coatings*.



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