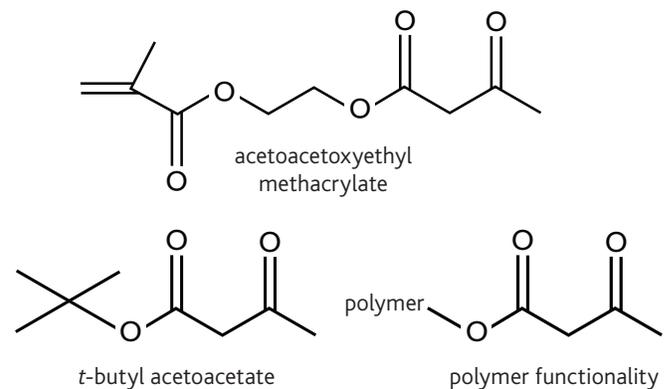


A method for suppressing yellow color in acetoacetate-melamine coating systems

Background

Acetoacetyl chemistry provides resin producers and coatings formulators with an additional tool for meeting strict VOC regulations while maintaining desirable resin and coating properties. The acetoacetate group may be incorporated into coatings resins in one of two ways: chain growth polymerization with Eastman™ AAEM (acetoacetoxyethyl methacrylate); or by direct reaction of hydroxyl-bearing polymers with Eastman™ *t*-BAA (*t*-butyl acetoacetate). Both of these intermediates and the resulting functionality of a polymer side chain are depicted in Figure 1. Not only can the acetoacetate group impart lower resin solution viscosity, it will also participate in various crosslinking reactions. These include both novel crosslinking mechanisms, such as enamine formation and Michael reaction, as well as conventional methods involving melamines and isocyanates. More detail on the synthesis and crosslinking pathways of acetoacetylated polymers can be found in Eastman publications N-319 and N-328.

Figure 1
Intermediate structures and polymer functionality



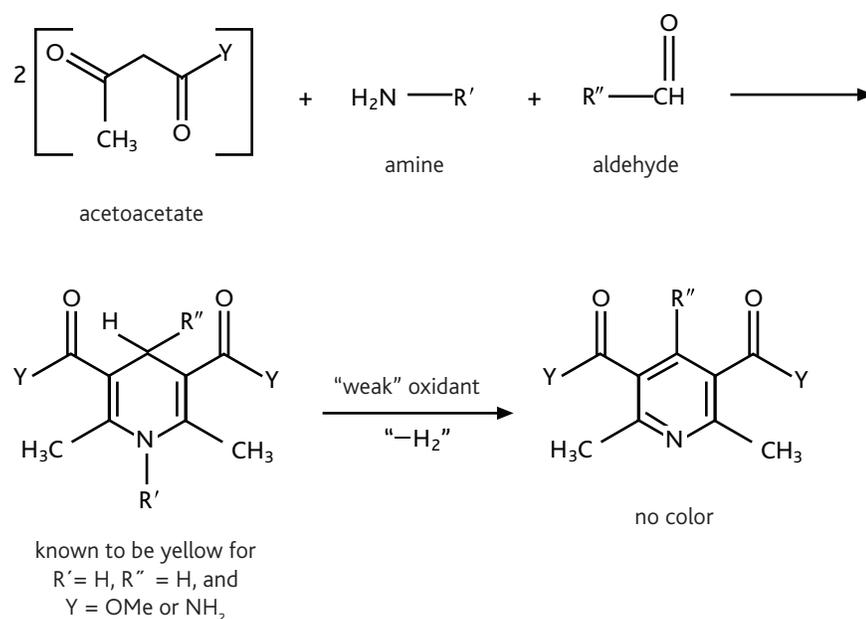
The acetoacetate group may undergo undesirable side reactions during storage of a formulated coating. These side reactions can lead to the formation of yellow chromophores, causing a visible yellow color in the coating. Work was performed to determine the possible origin of yellow color formation and how it might be prevented.

Origin of color—formation of dihydropyridines

The presence of an acetoacetate, a primary amine, and an aldehyde together in a coating solution may lead to the formation of substituted dihydropyridines, which are known to be yellow chromophores.

For example, combinations of either Eastman™ MAA (methyl acetoacetate) or acetoacetamide (β-keto butyramide, or BKB) with ammonia and formaldehyde will yield a yellow product. Figure 2 shows a possible reaction pathway producing

Figure 2
Reaction scheme for formation of dihydropyridines



For the experiment, it should be noted:

- Cases where $\text{R}' \neq \text{H}$ have not been investigated; only ammonia was studied.
- The full effect of Y, variance of the acetoacetate present, is unknown.
- The worst aldehyde is formaldehyde; for $\text{R}'' \neq \text{H}$ there is a blue shift in the UV-visible spectrum that dramatically decreases yellow color.
- If the inclusion of amines is necessary, tertiary amines, which cannot form dihydropyridines, should be used.
- The addition of weak oxidants may decrease or eliminate yellow color.

Evaluation of epoxide additives to suppress color formation

Experimental

Model systems analogous to coatings containing acetoacetate-functional resins and melamine crosslinkers were evaluated. Eastman™ EAA (ethyl acetoacetate) was used to simulate the acetoacetate resin. EAA was combined with typical melamine resins and acid catalysts. The total amount of melamine added provided an equal number of equivalents in each case. Testing indicates that the absence of either EAA, melamine, or acid catalyst prevents color formation.

The color of each solution was determined on a platinum cobalt color (Pt-Co) scale immediately after mixing. Since storage at elevated temperature accelerates yellow

color formation, each solution was held for 8 hours at 60°C (140°F). Afterwards, Pt-Co scale color was again determined for each solution.

Evaluation of various melamine crosslinkers

The type of melamine crosslinker was evaluated first. A series of seven solutions was tested; each contained a different commercially available melamine. The crosslinkers were chosen to provide a variety of alkylation types and degrees. Table 1 lists the melamines evaluated and the experimental results.

Table 1 Effect of melamine crosslinker on color development

Model system components:

- Eastman™ EAA (ethyl acetoacetate) 21.6 g
- *p*-TSA^a @ 20 wt% in *n*-butanol 2.2 g
- Melamine resin* **

Sample	*Melamine product	Type of melamine	**Amount, g	Final Pt-Co color ^b
1	Cymel™ 303 ^c	Fully methylated	65.0	150
2	Cymel 373	Partially methylated	76.5	300 ^d
3	Cymel 1133	Mixed ether (methyl/butyl)	65.0	70
4	Cymel 1156	Fully butylated	75.2	40
5	Cymel 327	High imino	72.2	50 ^e
6	Cymel 1172	Glycoluril	31.8	>500
7	Resimene™ ^f 747	Fully methylated	65.0	200

^a*p*-TSA = *p*-toluenesulfonic acid.

^bPlatinum-cobalt scale; reference ASTM D1209-84. A Pt-Co color of 200 is approximately a Gardner™ color of 1.

^cCytec

^dSample exhibited haze and white streaks after heating. Over time, sample increased in viscosity and eventually gelled.

^eSample exhibited noticeable viscosity increase after heating.

^fINEOS™ Melamines

Results show that color formation varies with the type of melamine crosslinker. The fully butylated melamine (Cymel 1156) exhibited the least color development, while the final colors of the partially methylated (Cymel 373) and glycoluril (Cymel 1172) were the most pronounced.

Evaluation of epoxide additives

The addition of small amounts of certain epoxide materials can reduce or eliminate color development in acetoacetate-melamine coatings. As a result, a series of model system solutions were formulated, each containing a different epoxide additive. These solutions were subjected to the same test methods described under Experimental. Table 2 lists those additives evaluated and their effect on color.

Table 2 Effect of epoxide additives on color development

Model system components

• Eastman™ EAA (ethyl acetoacetate)	21.6 g
• <i>p</i> -TSA @ 20 wt% in <i>n</i> -butanol	2.2 g
• Cymel™ 303 melamine resin	65.0 g
• Additive* (100%)	1.7 g

Sample	*Additive ^a	Final Pt-Co color ^b
1	None (control)	150
2	Limonene dioxide	10
3	Limonene monoxide	20
4	Limonene monoxide, 3.4 g	5
5	Vikoflex™ 7010	80
6	Alpha pinene oxide	100
7	Vikoflex™ 7170	150
8	Epoxy polybutene ^c	150

^aAll additives supplied by Elf Atochem.

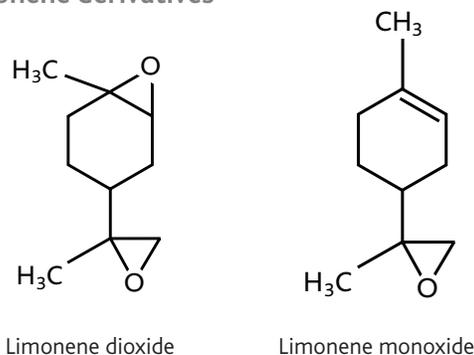
^bPlatinum-cobalt scale; reference ASTM D1209-84. A Pt-Co color of 200 is approximately a Gardner™ color of 1.

^cEpoxidized polybutadiene

Most of the epoxide additives inhibited color to some degree. The most effective color reduction per weight of additive was observed with limonene dioxide (LDO) and limonene monoxide (LMO). Since these two additives were the lowest molecular weight materials of the group, they possessed the lowest equivalent weights and number of epoxide groups per weight, as well. Figure 3 gives the structures of limonene dioxide and limonene monoxide.

Figure 3

Limonene derivatives



Since yellow color formation did not occur without the acid catalyst, it is believed these epoxide additives provide in situ blocking of the acid catalyst. This blocking effect may result in suppressing color development.

Evaluation of DDBSA and blocked DDBSA catalysts

Next, dodecylbenzenesulfonic acid (DDBSA) catalyst and an amine-blocked DDBSA catalyst were tested in place of *p*-TSA in the model system solutions. Each catalyst was evaluated with and without limonene dioxide additive. Table 3 gives the solution formulas and the results obtained.

Table 3 Effect of DDBSA and blocked DDBSA catalysts on color development

Components	Sample			
	1	2	3	4
Cymel™ 303	75.0 g	75.0 g	75.0 g	75.0 g
Eastman™ EAA	25.0 g	25.0 g	25.0 g	25.0 g
Blocked DDBSA catalyst ^a	0.5 g	0.5 g	—	—
Nacure™ 5076 ^b	—	—	0.5 g	0.5 g
Limonene dioxide	—	2.0 g	—	2.0 g
Initial Pt-Co color ^c	<10	<10	<10	<10
Final Pt-Co color	30	30	100	10

^aExperimental amine-blocked DDBSA catalyst (King Industries)

^bDDBSA catalyst

^cPlatinum-cobalt scale; reference ASTM D1209-84. A Pt-Co color of 200 is approximately a Gardner™ color of 1.

Results showed that, in solutions containing no epoxide additive, the experimental amine-blocked DDBSA catalyst offered the least color development. In addition, the limonene dioxide showed little effect with the blocked catalyst. However, the limonene dioxide was effective in suppressing color development with the unblocked DDBSA catalyst Nacure™ 5076.

Summary

- The combination of an acetoacetate, a primary amine, and an aldehyde may lead to the formation of colored dihydropyridines. It is suggested that this combination be avoided in a coating formulation; however, if an amine is necessary (i.e., for neutralizing acid catalysts), the use of a tertiary amine is suggested.
- The presence of an acetoacetate, a melamine crosslinker, formaldehyde, and an acid catalyst together in a coating may cause the solution to develop a yellow color on storage. Fully butylated Cymel 1156 yielded the least color development of the melamines evaluated. Conversely, partially methylated Cymel 373 and the glycoluril Cymel 1172 produced the strongest color development.
- The inclusion of 2–4 weight percent of an epoxide-functional additive in the model system solutions suppressed or eliminated color development. Both limonene dioxide and limonene monoxide were the most effective materials tested, by weight, for suppressing yellow color. The experimental amine-blocked DDBSA gave the least color development of the catalysts tested without an epoxide additive.

Conclusion

Experimentation has demonstrated the addition of an epoxide additive, particularly limonene dioxide, to a model coatings system was effective at suppressing the development of yellow color. It is believed the epoxide additives in these model systems led to in situ blocking of the acid catalyst. This would prevent the acid catalyst from promoting side reactions which produce yellow color bodies.



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