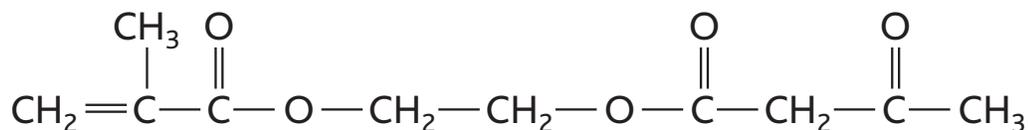


Waterborne acrylic emulsion formulation using Eastman™ acetoacetoxyethyl methacrylate (AAEM)



CAS No. 21282-97-3

Introduction

Stringent government regulations continue to be implemented for solvent emissions in the coatings industry. Waterborne acrylic emulsions are an option for achieving low-VOC industrial, architectural, and wood coatings. In addition, they offer advantages of high molecular weight, toughness, durability, and weatherability. Eastman™ AAEM monomer provides unique performance properties in emulsion-based coatings.

Advantages of Eastman™ AAEM in emulsion polymerization

- **Cross-linkable**—The active methylene and ketone carbonyl of Eastman AAEM will participate in numerous cross-linking reactions. These include novel cross-linking mechanisms such as enamine formation, Michael reaction, and aldehyde reaction, as well as conventional methods involving melamines and isocyanates (see Eastman publication N-319).
- **Improved adhesion to metals**—The ability of the acetoacetyl group to undergo chelation with metals increases adhesion of the binder to metallic substrates. Its effect has been demonstrated with improved corrosion resistance (see Eastman publication N-322).

The formulation and procedure presented in this publication demonstrate the utility of Eastman™ AAEM in an acrylic emulsion terpolymer. This formulation has not been optimized for any particular properties or application. It serves only as an example of how Eastman AAEM can be incorporated into an emulsion system. Alternative monomers, surfactant systems, and procedures should be considered to optimize for a particular application. Customers must decide for themselves the formulation that best suits their particular need.

Eastman™ AAEM acrylic emulsion terpolymer

A terpolymer consisting of butyl acrylate, methyl methacrylate, and Eastman AAEM can be prepared using a semicontinuous reaction process. Most of the water, all of the surfactant, and a portion of the monomer blend are charged to form a reaction heel. A small amount of initiator is added to the heel to generate polymer "seed" particles. This aids in establishing a uniform particle size distribution in the final product. The remaining monomer and initiator are added continuously to the reactor over time. Under these monomer-starved conditions, the opportunity for a runaway reaction is minimized. A small amount of buffer (sodium carbonate) is added to the reaction heel to neutralize the sulfuric acid generated as a by-product of the ammonium persulfate radical formation. The result is a final pH of 6–7, adding to the stability of the emulsion.

Formulation and preparation of the terpolymer are as follows:

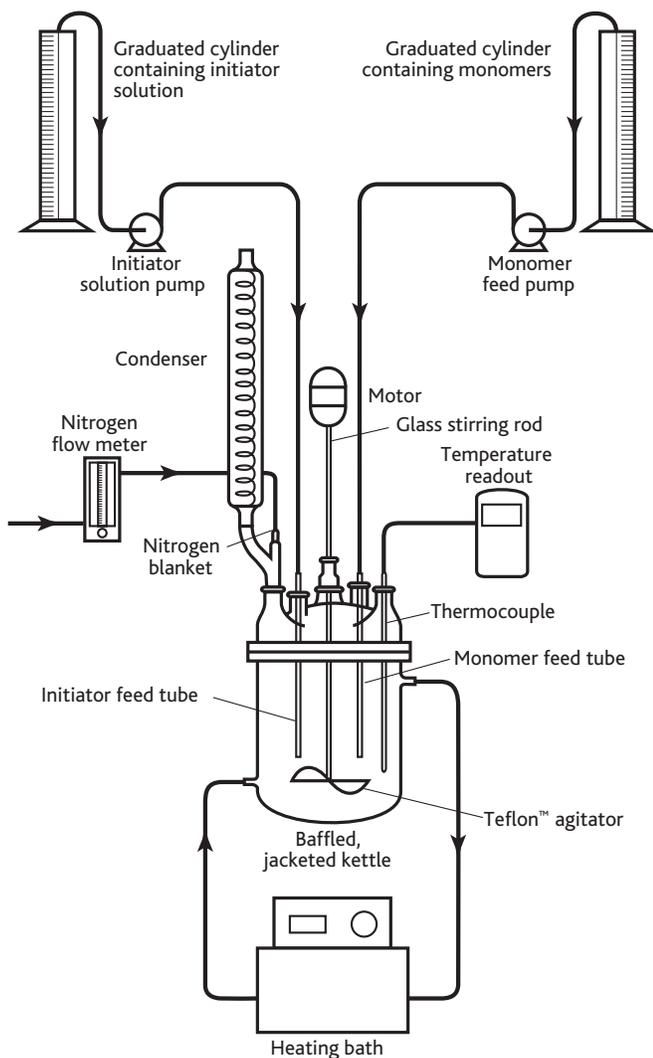
Table 1

Component	Wt%
Monomers	
Eastman™ AAEM	5.97
Butyl acrylate	12.89
Methyl methacrylate	20.92
Initiator	
Ammonium persulfate	0.04
Buffer	
Sodium carbonate	0.06
Surfactant	
Rhodapex™ CO-436 (solids only)	0.16
Distilled water	59.96

Procedure

1. Weigh the monomers into a suitable container and mix thoroughly.
 2. To form the initiator solution, dilute the ammonium persulfate in 25% of the total water quantity.
 3. Charge the remaining water, surfactant, and buffer in a jacketed kettle and heat to 80°C (176°F) using a circulating heating bath. A diagram of the emulsion synthesis apparatus is presented in Figure 1.
 4. When the solution reaches 80°C (176°F), add 10% of the monomer blend to the kettle and purge contents with nitrogen under gentle agitation. Monomer addition will cause the reactor temperature to decrease slightly. Convert the purge to a nitrogen blanket after the temperature of the contents returns to 80°C (176°F).
 5. Add 10% of the initiator solution to the kettle. Once a peak exotherm of 3°–4°C is achieved and the temperature begins to drop, begin the 3-hour subsurface feed of the monomer blend and the 3-hour, 20-minute subsurface feed of the initiator solution.
- Note:** Monitor the agitation rate to make sure the surface of the reactor is moving at all times. Increase as necessary.
6. Once initiator feed is complete, hold for an additional 40 minutes at 80°C (176°F) to reduce the amount of unreacted monomer. Cool to room temperature and filter. Total processing time from start of monomer feed to cooldown is approximately 4 hours.

Figure 1
Lab-scale emulsion synthesis apparatus



Emulsion properties characteristic of this formulation are given in Table 2.

Table 2 Typical properties of Eastman™ AAEM-modified acrylic emulsion terpolymer

Nonvolatiles, wt%	40
Molecular weight	
M _w , weight average	400,000
M _n , number average	100,000
Particle size, nm	100
Grit, ppm	<50
pH	6–7
T _g , °C by DSC	37

Film formation

Transparent, elastic films of the acrylic terpolymer were obtained through coalescence with Eastman Texanol™ ester alcohol. Various levels of Texanol, in parts per hundred (pph) based on polymer solids, were added to the emulsion, and its minimum film-forming temperature (MFFT) was determined. Figure 2 demonstrates how MFFT of the terpolymer drops with the addition of Texanol. Additional film properties are listed in Table 3.

Figure 2
Change in MFFT with addition of coalescing aid

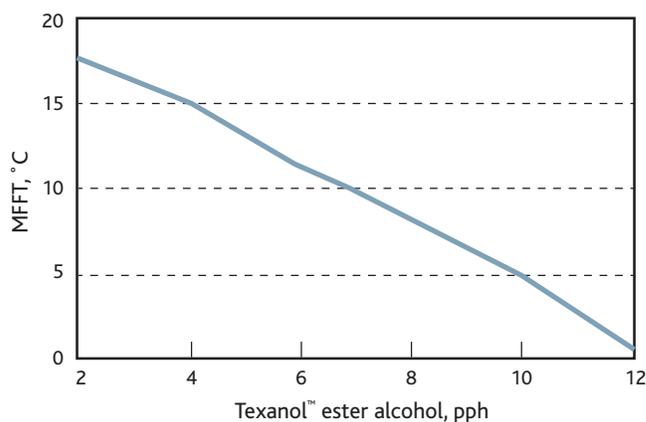


Table 3 Film properties^a of Eastman™ AAEM-modified acrylic emulsion terpolymer

MFFT, °C	7
Tensile strength, ^b psi	
@ Yield	200
Fracture	600

^aDetermined using film coalesced with 7.5 pph Eastman Texanol™ ester alcohol based on resin solids.

^bASTM D412.

Emulsion terpolymer stability

Package stability of the emulsion was evaluated under accelerated aging conditions in accordance with ASTM D1849-80 (Table 4). After 3 weeks at 52°C (125.6°F), the emulsion retained 90% of its initial pH without any settling or increase in gelled particles. Samples stored at ambient conditions have remained stable for more than 2 years.

Table 4 Package stability of Eastman™ AAEM-modified acrylic emulsion terpolymer under accelerated conditions at 52°C

Time (days)	Measured property ^a						
	Skinning	Pressure	Container corrosion	Odor of spoilage	Consistency (lumps)	pH	% pH retention
Initial	10	10	10	10	10	6.6	—
9	8	8	10	10	10	6.1	92.4
21	8	7	10	10	10	6.0	90.9

^aMeasured properties are defined by ASTM D1849-80 and rated by the following scale:

10 = none

8 = very slight

6 = slight

4 = moderate

2 = considerable

0 = complete failure

Summary

Eastman™ AAEM acrylic monomer has been successfully incorporated into acrylic polymers during emulsion polymerization. These waterborne emulsion polymers can then be formulated into low-VOC coatings. In addition, room-temperature cross-linking and improved adhesion to metallic substrates are imparted to the coating via the acetoacetyl functionality.

This area of polymer chemistry offers opportunities for coating manufacturers to achieve high-performance, environmentally acceptable coatings.

Raw material suppliers

AAEM	Eastman
<i>n</i> -Butyl acrylate	Dow
Methyl methacrylate	Dow
Ammonium persulfate	Aldrich
Sodium carbonate	Aldrich
Rhodapex™ CO-436	Rhone-Poulenc



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