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Eastman AAEM

Preventing hydrolysis during emulsion

Eastman acetoacetoxyethyl methacrylate (AAEM) is a specialty monomer used to improve the performance of, and provide unique properties to, acrylic emulsion. The main advantages of an AAEM-containing emulsion or emulsion film are:

- Improved block resistance, stain resistance, and water resistance via cross-linking
- Improved adhesion to metal substrate via chelating
- Improved formaldehyde (aldehyde) absorption functionality

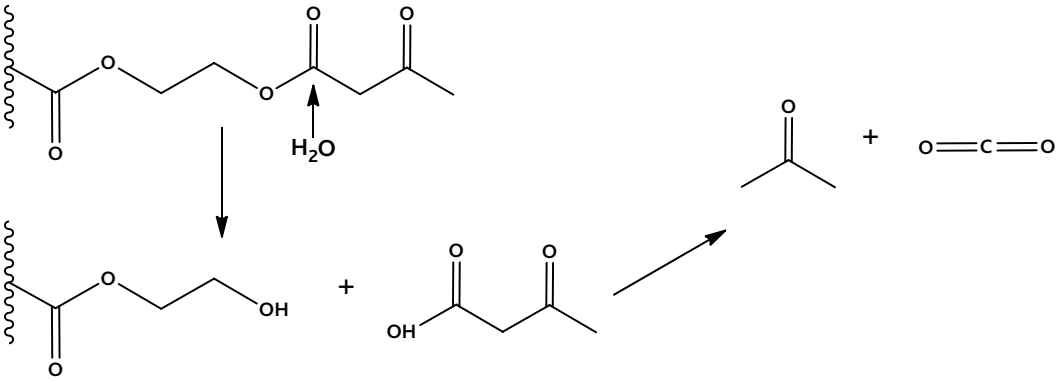
Eastman AAEM reacts easily with general acrylic monomers like methyl methacrylate, butyl acrylate, 2-ethylhexyl acrylate, and styrene monomer in both emulsion polymerization and bulk additional polymerization. See Table 1.

Table 1. Reactivity ratio

Monomer 1 (M1)	Monomer 2 (M2)	R1	R2
Eastman AAEM	Methyl methacrylate	0.95	0.90
Eastman AAEM	Styrene	0.60	0.70

The AAEM group in emulsion polymer runs the risk of hydrolysis, especially during storage, if it is not properly handled.

Figure 2. AAEM hydrolysis reaction

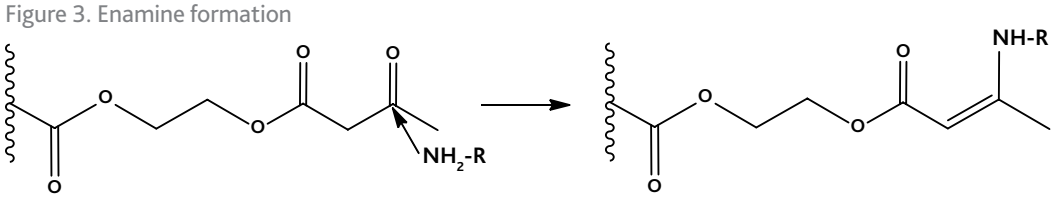


As shown in Figure 2, the AAEM group on the polymer chain will be hydrolyzed to hydroxyethyl methacrylate (HEMA) and β-keto acid. The β-keto acid will further degrade to acetone and carbon dioxide (CO_2).

Hydrolysis reaction is greatly affected by temperature, resulting in latex being synthesized and stored. Higher temperatures result in the AAEM group being hydrolyzed faster.

Results show that by adding an amine, especially a less steric hindered primary amine, an enamine structure can be formed. The structure from experimental data, shown in Figure 3, is more resistant to hydrolysis. Basically, when more amines are added, the structure is able to develop stronger protection.

Figure 3. Enamine formation



The following practices listed are suggestions for synthesizing and storing an AAEM emulsion:

1. Balance emulsion polymerization temperature and time to avoid AAEM exposure to high temperatures over a longer period of time. Add AAEM monomer at a later stage of the polymerization process. For example, add AAEM to monomer tank after 50% of monomer feed.
2. At the end of the process, add amine neutralizer to adjust the pH of emulsion above 8.5; the higher, the better. Less sterically hindered primary amine is recommended.
    a. Examples of amine are ammonia hydroxide and monoethanolamine.
    b. Note that secondary and tertiary amines are not recommended.
    c. Sterically hindered primary amines, such as 2-amino-2-methyl-1-propanol, are also not recommended.
3. Avoid storing emulsion products containing AAEM at high temperatures. Store at a temperature no higher than 23° ± 2°C.

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