EASTMAN

Eastman copromoters
for effective polyester cure

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Eastman copromoters provide a complete and rapid cure response in the room-temperature cure of unsaturated polyester resins. They also impart relatively low initial color to cured polyesters; however, since copromoters in general may affect color stability after extended weathering, applications requiring optimum color retention should be evaluated prior to use. *N,N*-dimethylacetoacetamide (DMAA), ethyl acetoacetate (EAA), and methyl acetoacetate (MAA) are noted for their lower level of toxicity and ease of handling when compared with common amine copromoters such as dimethylaniline (DMA).

Effective cure at room temperature

Unsaturated polyester resins are cured by a free-radical addition reaction. The reaction is initiated by the use of a peroxide compound that produces free radicals when heated or in the presence of a promoter at room temperature.

The two primary room-temperature cure systems are based on either benzoyl peroxide (BPO) or methyl ethyl ketone peroxide (MEKP). BPO is most often promoted with DMA. MEKP is frequently promoted with a complex of cobalt (e.g., naphthenate or octoate) and can be copromoted.

The MEKP/metal complex is easily adapted to various types of fabrication processes and is more widely used than BPO systems. Copromoters are used to facilitate the cure of MEKP-initiated reactions. Eastman copromoters function by coordination with the cobalt promoter. They are not recommended for BPO-initiated cure systems, which do not use metal complexes for promotion. Without a copromoter, the MEKP system may require long production cycles or may fail to provide a complete cure, thus limiting the performance of the polyester.

Table 1. Eastman copromoters: lower color and lower toxicity than DMA

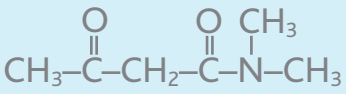
	EAA	MAA	AAA	DMAA	DMA
Health hazard rating (3 = most hazardous)					
HMIS[a]	2	3	2	1	3
NFPA[b]	2	2	2	1	3
Color imparted to resin	Low	Low	Low	Low	High
Physical form	Water-white liquid	Water-white liquid	White powder	20% aqueous solution (pink-yellow)	Yellow liquid
Effectiveness (5 = most effective)	1	1	2	3	5

[a] *Hazardous Materials Identification System. See safety data sheet for explanation.*

[b] *National Fire Protection Association. See safety data sheet for explanation.*

DMAA

DMAA can be used as a general-purpose copromoter in most unsaturated polyester resin formulations. This compound is effective for resins based on various combinations of propylene glycol (PG), NPG glycol, TMPD glycol, bisphenol A, phthalic anhydride (PA), isophthalic acid (IPA), and maleic anhydride (MA). Data in Tables 3–6 demonstrate the effectiveness of DMAA compared with DMA as a copromoter for several different unsaturated polyester resin formulations. Data in Table 3 indicates that DMAA at 0.3 wt% is comparable to DMA at 0.1 wt% in PG/PA/MA and PG/IPA/MA resins. DMAA is slightly more effective than DMA at equal concentrations in a bisphenol A resin (Table 3), and the DMAA concentration can be increased in this system to obtain better overall cure. Although DMAA is supplied as an aqueous solution, no detrimental effects on cured polyester were noted during evaluations conducted in Eastman laboratories.



N,N-dimethylacetoacetamide

CAS No. 2044-64-6

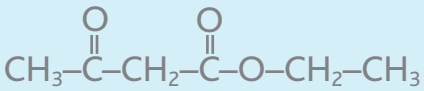
Molecular weight: 129.2

Empirical formula: $C_6H_{11}NO_2$

EAA

EAA and MAA are low-color, low-viscosity liquids that are readily soluble in styrenated resins. They are approximately equal in effectiveness as copromoters. The data in Table 3 compare EAA and DMA as copromoters for three unsaturated polyester resins and show that EAA must be used at higher concentrations than DMA to approach equal effectiveness. Some resins may require EAA or MAA concentrations as high as 1 wt% to obtain effective cure development. Unsaturated polyester resins copromoted with EAA or MAA have lower color than those which use DMA (Figure 1), providing a distinct advantage in many applications.

Because they are difficult to cure, most styrenated bisphenol A resins are copromoted. The data in Table 3 compare the effectiveness of DMA, EAA, and MAA as copromoters for a styrenated bisphenol A resin. The data indicate that bisphenol A resins copromoted with EAA or MAA develop desirable hardness more rapidly than resins copromoted with DMA at equivalent concentration. Extended gel times are also obtained with EAA or MAA compared with DMA. At the same time, EAA or MAA will provide the slower gel times that are necessary for most fabrication processes.



Ethyl acetoacetate

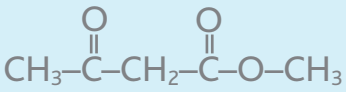
CAS No. 141-97-9

Molecular weight: 130.1

Empirical formula: $C_6H_{10}O_2$

MAA

Eastman copromoters, which are acetoacetates, do not contain an amine group in the molecular structure; therefore, they do not impart brown color to the polyesters as amine promoters do. Toxicity tests of MAA and EAA reveal that they constitute relatively low hazards by inhalation and skin contact.



Methyl acetoacetate

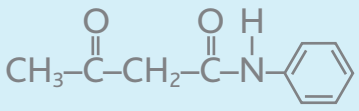
CAS No. 105-45-3

Molecular weight: 116.1

Empirical formula: $C_5H_8O_3$

AAA

AAA is a white powder that is soluble in styrenated resins; however, agitation for 1 to 2 hours may be required for complete solution at room temperature. AAA is also soluble (up to about 40%) in DMAA and has been used in a 70/30 ratio of DMAA/AAA. Data in Table 3 show the effectiveness of a DMAA/AAA solution compared with DMA as a copromoter for four unsaturated polyester resins. The information indicates that the DMAA/AAA blend at 0.3 wt% level is comparable to DMA at 0.1 wt% level in PG/PA/MA and PG/IPA/MA resins. DMAA/AAA is superior to DMA at equal concentrations in a resin prepared from NPG glycol/IPA/MA and in a bisphenol A resin.



Acetoacetanilide

CAS No. 102-01-2

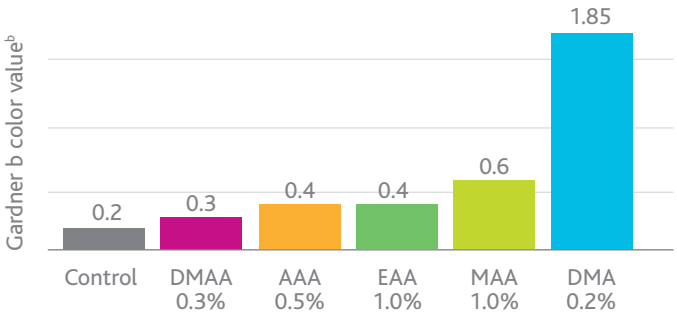
Molecular weight: 177.2

Empirical formula: $C_{10}H_{11}NO_2$

Eastman copromoters impart lower initial color to cured polyester systems

The effect of various Eastman copromoters on the initial color of a cured white gel-coat system is compared with that of DMA in Figure 1. The information clearly demonstrates that the Gardner b color value of gel coats cured with Eastman copromoters is no more than one-third of those produced with similar systems copromoted with DMA, which is used at lower concentrations.

Figure 1. Effect of various copromoters on the color of a cured white gel coat[a]



[a] *NPG glycol/IPA/MA (1:1) resin containing 45% styrene. Gel coat prepared with 20% TIO_2 and 1.5% fumed silica (thixotropic agent).*

[b] *Degree of yellowness.*

Summary

Eastman copromoters are useful in the MEKP-initiated room-temperature cure of unsaturated polyester resins, particularly in specialty resin formulations based on NPG glycol, TMPD glycol, propylene glycol, and bisphenol A. Since the overall performance of an unsaturated polyester resin depends on many variables, Eastman suggests that producers/fabricators use this information as a guide. By applying your own technology, you may receive the benefits of long pot life, extended gel time, good cure, low color, and relatively low toxicity that the Eastman copromoters offer.

Warning

Catalyst (methyl ethyl ketone peroxide) must never be mixed directly with promoters (cobalt octoate or naphthenate) or copromoters (*N,N*-dimethylacetoacetamide, acetoacetanilide, ethyl acetoacetate, or methyl acetoacetate) because violent decomposition may occur. The catalyst and promoters must always be added separately to the polyester resin. The order of addition should be to add the promoter(s) first, followed by the catalyst. Care must be taken to thoroughly mix the promoter(s) with the resin before adding the catalyst.

Table 2. Eastman copromoters[a]

	DMAA	EAA	MAA	AAA
Physical form	Liquid	Liquid	Liquid	Powder
Assay, wt%	79–83	99.5	99	99.5
Molecular weight	129.2	130.14	116.12	177.2
Color	350 Pt-Co	15 Pt-Co	25 Pt-Co	White to off-white
Suggested concentration, wt%	0.2–0.5	0.3–1.0	0.3–1.0	0.3–0.7
Comments on use	General-purpose copromoter. Low color.	Low color. Excellent in bisphenol A resins.	Similar to EAA	Must be agitated for dissolution in styrene. Soluble to 40% in DMAA.

[a] *Properties reported here are typical of average lots. Eastman makes no representation that the material in any particular shipment will conform exactly to the values given.*

Table 3. Cure development with various copromoters

	Cure system[a] 6%			Cure parameters			Barcol hardness development[b]		
	Copromoter	Cobalt	MEKP	GT, min	TPE, min	PE, °C (°F)	1 h	2 h	24 h
PG/PA/MA resin (42% styrene—300 ppm Eastman hydroquinone)									
DMA	0.1	0.3	1.0	8.2	3.5	177 (350)	37	40	40
DMAA	0.3	0.3	1.0	10.8	5.0	174 (345)	37	38	40
DMAA/AAA[c]	0.3	0.3	1.0	10.2	6.0	180 (355)	40	40	40
EAA	0.5	0.3	1.0	21.3	8.0	174 (345)	10	25	25
PG/IPA/MA resin (42.5% styrene—250 ppm Eastman hydroquinone)									
DMA	0.1	0.4	1.0	7.2	3.0	185 (365)	40	40	40
DMA	0.3	0.4	1.0	5.0	2.5	152 (305)	25	30	30
DMAA	0.3	0.4	1.0	7.2	3.5	188 (370)	40	40	40
DMAA	0.5	0.4	1.0	5.2	3.0	193 (380)	40	40	44
DMAA/AAA[c]	0.3	0.4	1.0	8.9	4.0	185 (365)	40	40	40
EAA	0.5	0.4	1.0	19.5	3.0	157 (315)	40	40	40
Resin based on NPG glycol/IPA/MA resin (45% styrene—300 ppm Eastman hydroquinone)									
DMA	0.3	0.5	1.0	7.5	5.0	160 (320)	20	20	20
DMAA	0.3	0.5	1.0	13.1	5.0	185 (365)	40	40	40
DMAA/AAA[c]	0.3	0.5	1.0	12.8	7.0	180 (355)	35	35	40
EAA	0.5	0.5	1.0	25.9	9.0	177 (350)	0	0	10
Bisphenol A resin (commercial, unpromoted resin—50% styrene—100 ppm Eastman hydroquinone)									
DMA	0.3	0.8	1.5	4.6	3.0	174 (345)	10	10	10
DMAA	0.3	0.8	1.5	4.4	4.5	182 (360)	15	15	15
DMAA	0.5	0.8	1.5	2.6	4.0	185 (365)	30	35	35
DMAA/AAA[c]	0.3	0.8	1.5	5.1	6.0	182 (360)	20	20	20
EAA	0.3	0.8	1.5	22.2	9.0	185 (365)	20	25–30	30
MAA	0.3	0.8	1.5	22.5	7.0	182 (360)	30	30	30

[a] *Values given are weight percent concentrations.*

[b] *Barcol hardness measures were made on 50-g cured resin samples in half-gallon paint can lids.*

[c] *70:30 ratio*

Product legend

IPA Isophthalic acid

MA Maleic anhydride

PA Phthalic anhydride

PG Propylene glycol

Cure legend (50 g resin in a paper cup)

GT Gel time

PE Peak exotherm temperature

TPE Time to peak exotherm after gel

For more information, see Eastman publication ADD-3126, *Eastman inhibitors for the fiberglass-reinforced plastics market*.

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