

Eastman inhibitors for the fiberglass-reinforced plastics market

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Inhibitors based on hydroquinone are used to control the cure characteristics of unsaturated polyester/vinyl monomer blends.

Inhibitors are selected based on their ability to:

- Prevent gelation of the unsaturated polyester during the esterification reaction
- Prevent gelation during blending of the polyester with the vinyl monomer at elevated temperature
- Impart good shelf life to the resin
- Aid in adjusting gel time
- Exert a minimum effect on subsequent curing of the resin after gelation

No single inhibitor has all of these attributes; therefore, a combination of inhibitors is normally used to achieve a balance of desired properties. The performance of an inhibitor or blend of inhibitors is also influenced by the structure and reactivity of the polyester resin.

Eastman inhibitors

Hydroquinone (HQ)

HQ is the lowest cost and most commonly used inhibitor in this series. It is very effective at protecting resins during roomtemperature storage and extending gel time. For elevated temperature use, HQ is inferior to some of its derivatives.

Toluhydroquinone (THQ)

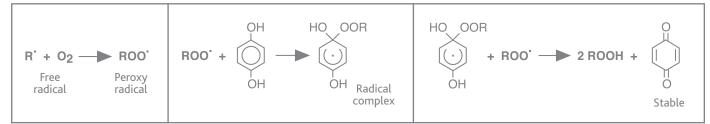
THQ is an effective process inhibitor in the production of highly reactive unsaturated polyesters.

Mono-tert-butylhydroquinone (MTBHQ)

MTBHQ is an effective storage inhibitor for unsaturated polyesters and is also useful as a cook stabilizer for highly reactive, unsaturated polyesters. MTBHQ is probably the best all-around inhibitor, offering excellent potency over a wide temperature range and causing only moderate prolongation of resin cure at elevated temperatures.

2,5-Di-tert-butylhydroquinone (DTBHQ)

DTBHQ can be used to provide improved storage stability for unsaturated polyesters. The hindered reactive groups cause DTBHQ to react with free radicals slowly and over a long period of time. While this rate of reactivity is sufficient to scavenge the free radicals that occur in storage, it does not effectively scavenge the free radicals that are generated during cure. Thus DTBHQ can be used to increase package stability with minimal effect on gel time.



Inhibitor mechanism

Hydroquinone and hydroquinone derivatives, with the exception of *p*-benzoquinone, require the presence of oxygen to effectively inhibit the propagation of free radicals. These free radicals react with oxygen to form peroxy radicals, two of which oxidize the hydroquinone to benzoquinone via an intermediate hemiketal radical complex. The free radicals are thus reduced to hydroperoxides.

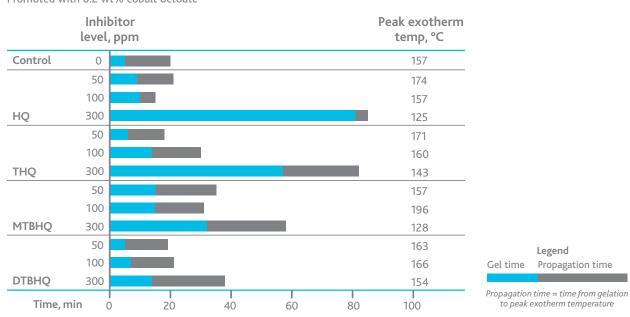
Inhibitor effectiveness¹

For the same cure package of catalyst, promotor, and inhibitor, cure response can vary drastically between resins of different compositions or reactivities. To demonstrate this, gel time studies were performed on various resins, changing the inhibitor type and level while maintaining catalyst and promotor levels. Data in Figures 1 through 5 demonstrate the effectiveness of hydroquinone inhibitors in prolonging gel time and propagation time in room-temperature-cured systems. Figure 6 and Figure 7 contain information on systems cured at elevated temperatures. For the systems cured with benzoyl peroxide, commercially produced polyester resins were used. For the systems cured with MEK peroxide, carefully controlled resins were prepared on a laboratory scale in Eastman's technical service laboratories. In each series, the compositions were selected to provide a range of reactivities. In all cases, styrene was used as the vinyl monomer reactive diluent.

¹ It is often more desirable to add a concentrated solution of inhibitor rather than directly add the solid inhibitor to the resin solution. For this reason, stock solutions in concentrations of 1–10 wt% or higher are prepared in the monomers or solvents listed in Table 2. Prolonged storage can result in discoloration and diminished effectiveness of stock solutions.

Room-temperature cure with MEKP

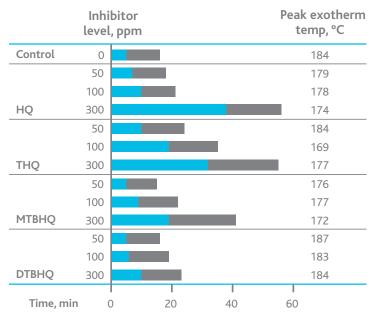
Figure 1. PG/PA/MA 1:1 at various inhibitor levels^a Initiated with 1.0 wt% MEKP Promoted with 0.2 wt% cobalt octoate



^a PG = propylene glycol. PA = phthalic anhydride. MA = maleic anhydride.

Room-temperature cure with MEKP

Figure 2. PG/PA/MA 1:3 at various inhibitor levels^a Initiated with 1.0 wt% MEKP Promoted with 0.2 wt% cobalt octoate

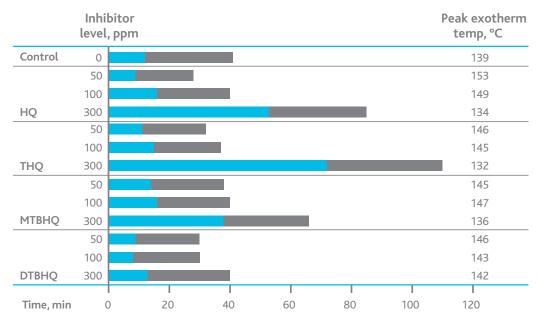


Legend				
Gel time	Propagation time			

Propagation time = time from gelation to peak exotherm temperature

^a *PG* = *propylene glycol*. *PA* = *phthalic anhydride*. *MA* = *maleic anhydride*.

Figure 3. Eastman NPG[™] glycol/PA/MA 1:3 at various inhibitor levels^a Initiated with 1.0 wt% MEKP Promoted with 0.2 wt% cobalt octoate



^a PG = propylene glycol. PA = phthalic anhydride. MA = maleic anhydride.

Room-temperature cure with BPO

133

152

136

121

100

Peak exotherm Inhibitor level, ppm temp, °C Control 0 169 50 154 100 133 HQ 300 124 50 146 100 135 THQ 300 143 50 149 100 132

40

60

80

Legend Gel time Propagation time

Propagation time = time from gelation to peak exotherm temperature

^a *PG* = propylene glycol. *PA* = phthalic anhydride. *MA* = maleic anhydride.

20

Figure 5. PG/PA/MA 1:3 at various inhibitor levels^a Initiated with 1 wt% benzoyl peroxide Promoted with 0.5 wt% dimethylaniline

MTBHQ

DTBHQ

Time, min

300

50

100

300

0

Inhibitor level, ppm				k exotherm emp, °C		
Control	0					196
	50					183
	100					178
HQ	300					171
	50					193
	100					183
THQ	300					183
	50					185
	100					185
MTBHQ	300					186
	50					175
	100					185
DTBHQ	300					183
Time, mi	n	0	20	40	60	

^a *PG* = propylene glycol. *PA* = phthalic anhydride. *MA* = maleic anhydride.

Figure 4. PG/PA/MA 1:1.5 at various inhibitor levels^a Initiated with 1 wt% benzoyl peroxide Promoted with 0.5 wt% dimethylaniline

Elevated-temperature cure with BPO

SPI exotherm test @ 82°C (180°F)

	Inhibitor level, ppm		Peak exotherm temp, °C		
Control	0		204		
	50		204		
	100		192		
HQ	300		177		
	50		204		
	100		195		
THQ	300		191		
	50		193		
	100		188		
MTBHQ	300		193		
	50		204		
	100		195		
DTBHQ	300		185		
Time,	min	0	1 20		

Figure 6. PG/PA/MA 1:1.5 at various inhibitor levels^a Initiated with 1 wt% benzoyl peroxide

Figure 7. PG/PA/MA 1:3 at various inhibitor levels^a Initiated with 1 wt% benzoyl peroxide

^a *PG* = propylene glycol. *PA* = phthalic anhydride. *MA* = maleic anhydride.

^a *PG* = propylene glycol. *PA* = phthalic anhydride. *MA* = maleic anhydride.

Legend Gel time Propagation time

Propagation time = time from gelation to peak exotherm temperature For inhibitor levels evaluated at elevated temperature and higher-reactivity resins cured with MEKP at room temperature, THQ was the most effective at prolonging gel time and propagation time. In room-temperature-cured, moderate-reactivity resins based on PG and Eastman NPG[™] glycol, MTBHQ appeared to provide the longest gel time extension and propagation time at lower inhibitor levels. DTBHQ provided the least gel and propagation time extension.

	OH OH	OH OH OH	OH C(CH ₃) ₃ OH	^{OH} ₃ (CH ₃)C
	HQ ^c	THQ	МТВНО	DTBHQ
Empirical formula	C ₆ H ₆ O ₂	C ₇ H ₈ O ₂	C ₁₀ H ₁₄ O ₂	C ₁₄ H ₂₂ O ₂
Molecular weight	110.11	124.13	166.21	222.31
Physical form	Crystals	Crystals	Crystals	Crystals
Color	White to light tan	White to tan	Tan	White to tan
Specific gravity	1.328	1.336	1.05	1.07
Bulk density, g/mL	0.66	0.60	0.22	0.61
Assay, wt%	99.0	99.0	98.0	99.0
Water, wt%	1.00	0.04	1.10	0.03
Melting point, °C	169	128	125	215
Boiling point, °C	286	285	295	313
Flash point, ^d °C	177	172	171	216
Fire point, °C	191	177	174	216
Autoignition temp., °C	499	452	457	421

Table 1. Typical properties of Eastman hydroquinone and derivatives^{a,b}

^a Reported for information only. Eastman makes no representation that material in any particular shipment will conform to the values listed.

^b Typical property bulletins are available for all grades of hydroquinone and derivatives.

^c Eastman offers 2 grades of hydroquinone: USP and photographic.

^d Cleveland open cup

Table 2. Approximate solubility in vinyl monomers and various solvents^{a,b}

	HQ ^c	мтвно	DTBHQ	THQ
Styrene	<5	<5	<5	<5
Methyl methacrylate	5	41	19	16
Propylene glycol	23	41	10	26
Eastman EEP solvent	14	52	25	28
Triethyl phosphate	32	41	10	41

^a Reported for information only. Eastman makes no representation that material in any particular shipment will conform to the values listed.

^b Inhibitor was added in increments of 1 wt% and evaluated for solubility after 24 hours at ambient temperature.

^c Eastman offers 2 grades of hydroquinone: USP and photographic.

Additional information on cure control is available in Eastman publication ADD-3125, *Eastman copromoters for effective polyester cure*.



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