EASTMAN

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 room-temperature 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.

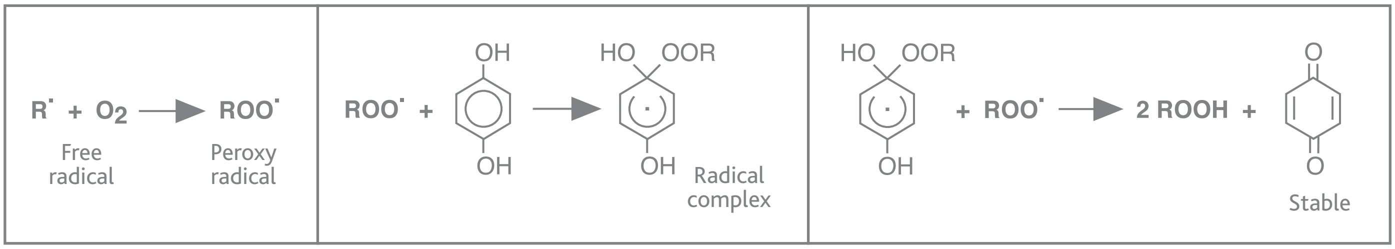
Mono-tert-butylhydroquinone (MTBHQ)

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.

Proposed inhibitor mechanism with hydroquinone



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 effectiveness[1]

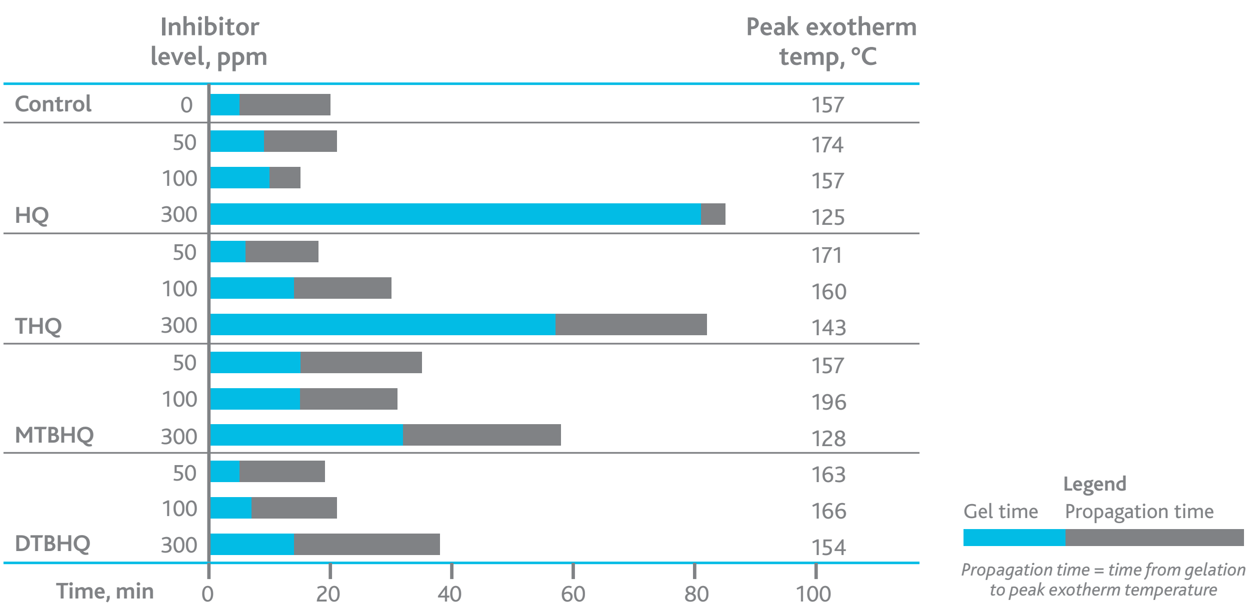
For the same cure package of catalyst, promotor, and inhibitor, cure response can vary drastically between resins of different compositions or reactivities. To demonstrate this, gel time studies were performed on various resins, changing the inhibitor type and level while maintaining catalyst and promotor 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.*

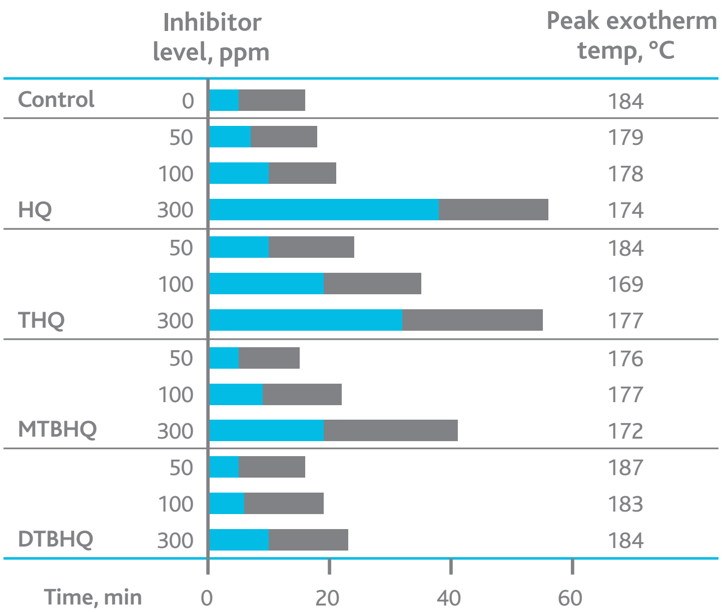
Room-temperature cure with MEKP

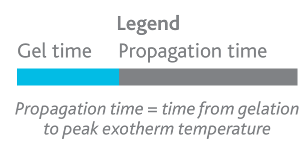
Figure 1. PG/PA/MA 1:1 at various inhibitor levels[a]
Initiated with 1.0 wt% MEKP
Promoted with 0.2 wt% cobalt octoate



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

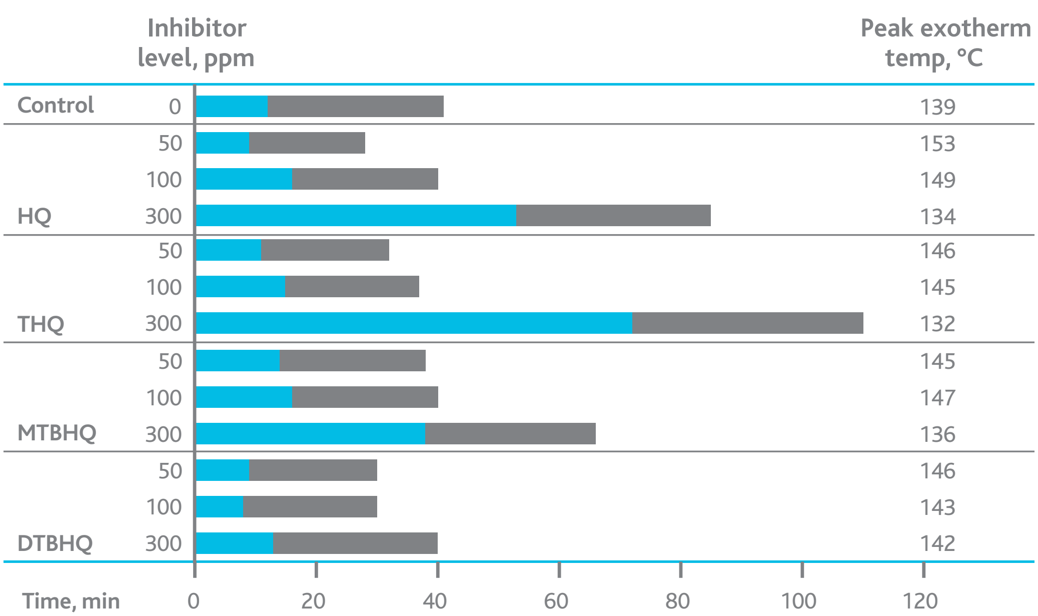
Figure 2. PG/PA/MA 1:3 at various inhibitor levels[a]
Initiated with 1.0 wt% MEKP
Promoted with 0.2 wt% cobalt octoate





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

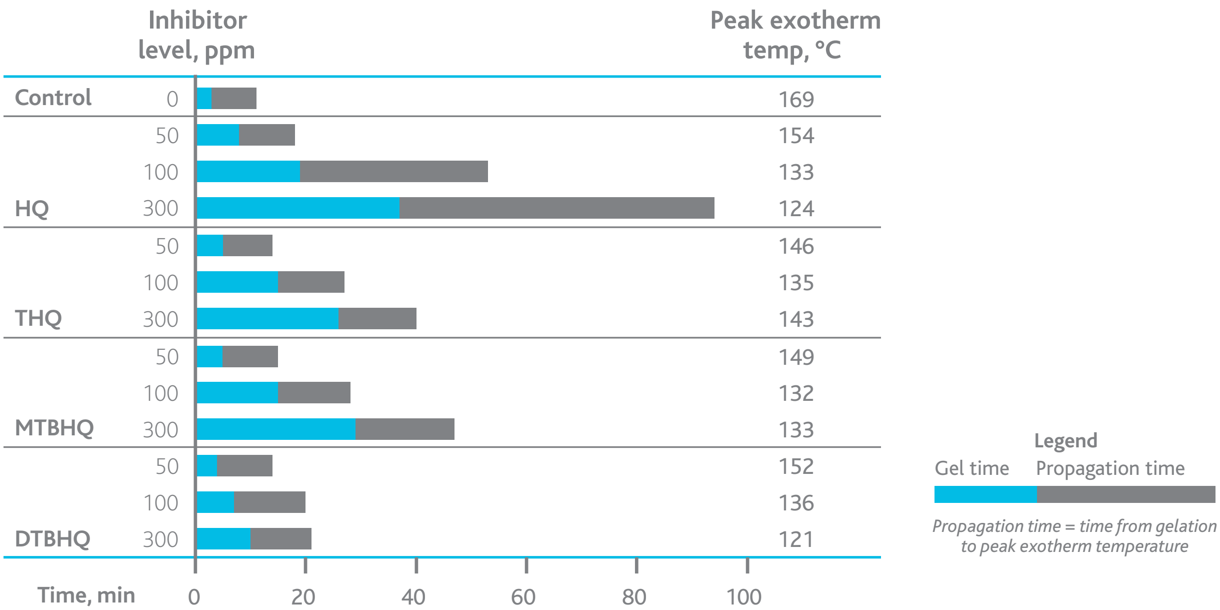
Figure 3. Eastman NPG™ glycol/PA/MA 1:3 at various inhibitor levels[a]
Initiated with 1.0 wt% MEKP
Promoted with 0.2 wt% cobalt octoate



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

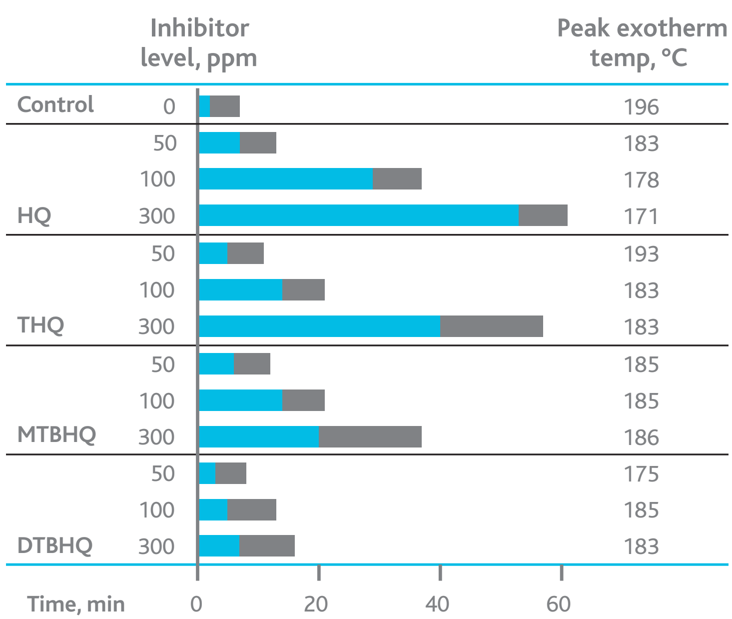
Room-temperature cure with BPO

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



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

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



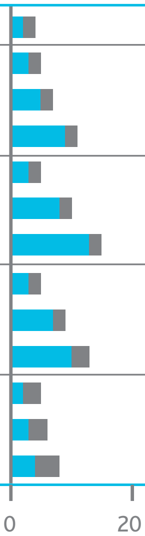
[a] *PG = propylene glycol. PA = phthalic anhydride. MA = maleic anhydride.*

Elevated-temperature cure with BPO

SPI exotherm test @ 82°C (180°F)

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

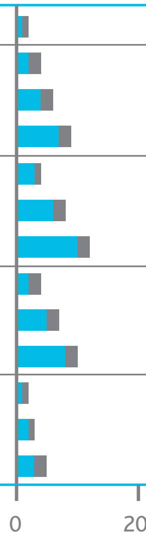
	Inhibitor level, ppm	Peak exotherm temp, °C
Control	0	204
	50	204
	100	192
HQ	300	177
	50	204
	100	195
THQ	300	191
	50	193
	100	188
MTBHQ	300	193
	50	204
	100	195
DTBHQ	300	185



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

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

	Inhibitor level, ppm	Peak exotherm temp, °C
Control	0	233
	50	236
	100	232
HQ	300	229
	50	236
	100	230
THQ	300	227
	50	232
	100	229
MTBHQ	300	229
	50	232
	100	229
DTBHQ	300	228



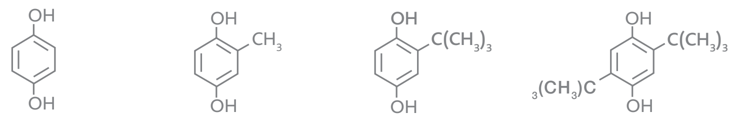
[a] *PG = propylene glycol. PA = phthalic anhydride. MA = maleic anhydride.*

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.

Table 1. Typical properties of Eastman hydroquinone and derivatives[a,b]



	HQ[c]	THQ	MTBHQ	DTBHQ
Empirical formula	$C_6H_6O_2$	$C_7H_8O_2$	$C_{10}H_{14}O_2$	$C_{14}H_{22}O_2$
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

[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]	MTBHQ	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.*

EASTMAN
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