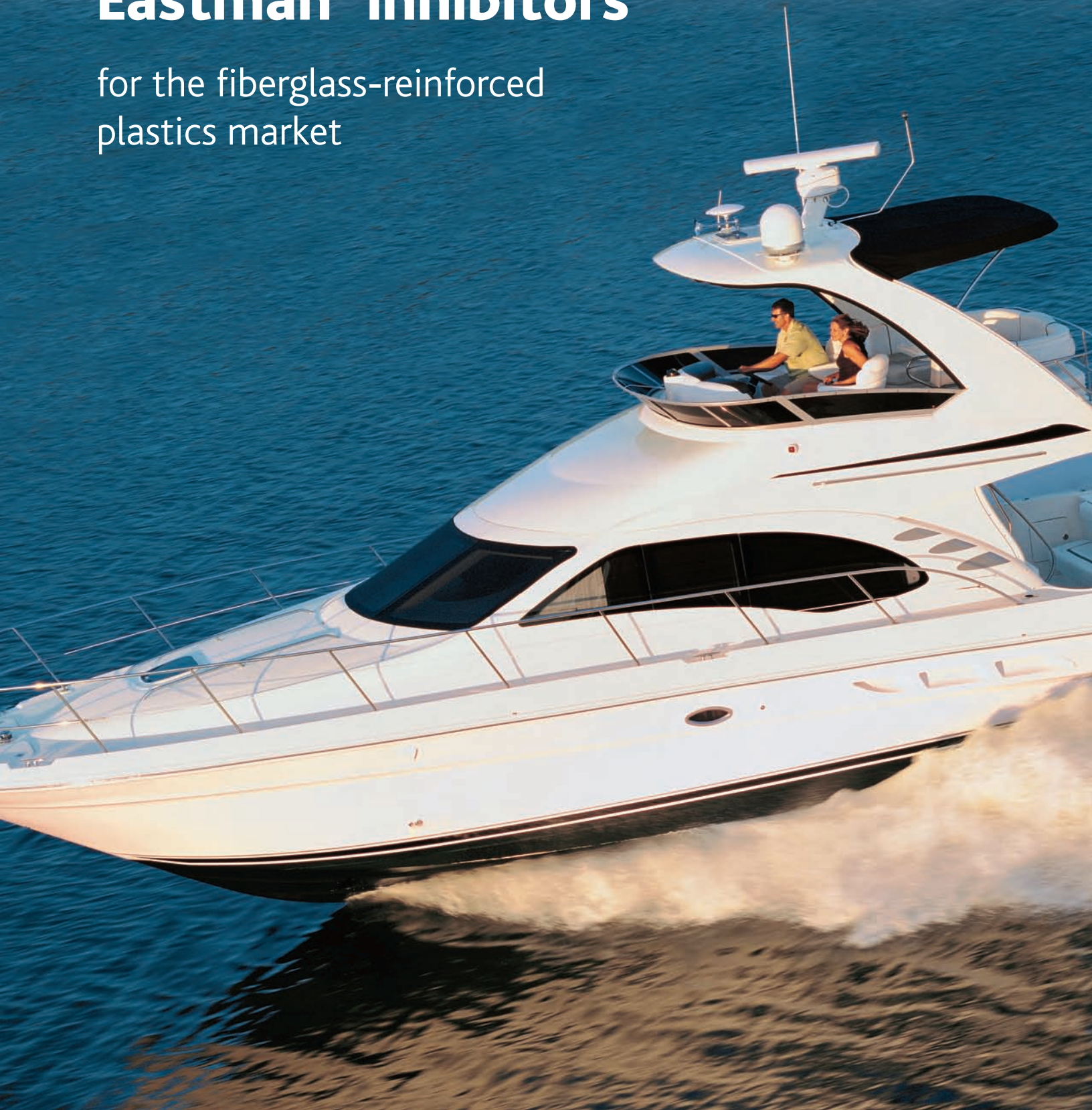


**EASTMAN**

# Eastman™ inhibitors

for the fiberglass-reinforced  
plastics market



# Eastman™ inhibitors for the fiberglass-reinforced plastics market

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 at 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.

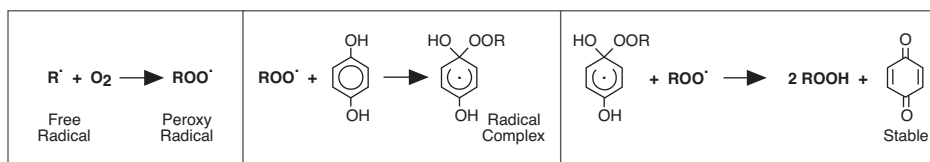
### 2,5-Di-tert-Butylhydroquinone (2,5-DTBHQ)

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 hemi-ketal radical-complex. The free radicals are thus reduced to hydroperoxides.

### Proposed inhibitor mechanism with hydroquinone



## Inhibitor effectiveness<sup>1</sup>

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.

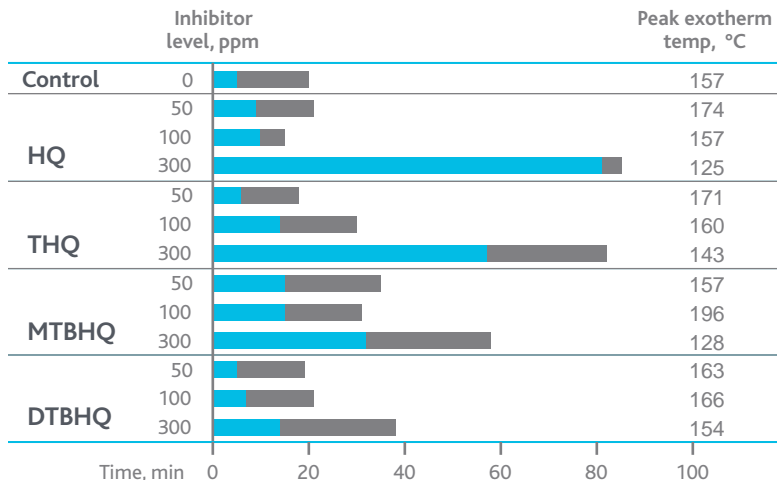
Figures 6 and 7 contain information on systems cured at elevated temperatures. For the systems cured with benzoyl peroxide, commercially produced polyester resins were used. For the systems cured with MEK peroxide, carefully controlled resins were prepared on a laboratory scale in Eastman's technical 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.

<sup>1</sup>It is often more desirable to add a concentrated solution of inhibitor rather than to 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

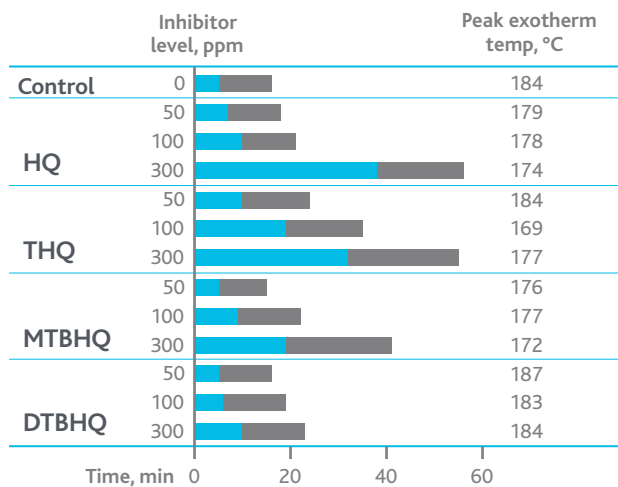
**Figure 1 (PG/PA/MA 1:1) at various inhibitor levels<sup>a</sup>**

Initiated with 1.0 wt % MEKP  
Promoted with 0.2 wt % cobalt octoate



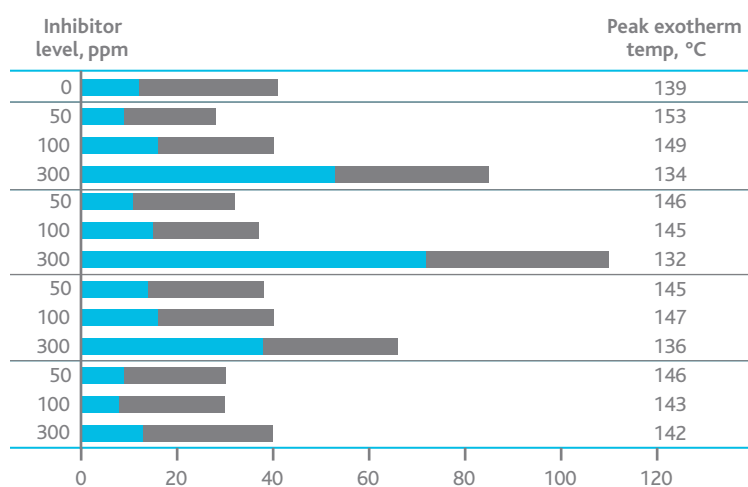
**Figure 2 (PG/PA/MA 1:3) at various inhibitor levels<sup>a</sup>**

Initiated with 1.0 wt % MEKP  
Promoted with 0.2 wt % cobalt octoate



**Figure 3 (Eastman NPG™/PIA/MA 1:1) at various inhibitor levels<sup>a</sup>**

Initiated with 1.0 wt % MEKP  
Promoted with 0.2 wt % cobalt octoate



<sup>a</sup>PG = propylene glycol. PA = phthalic anhydride. MA = maleic anhydride.

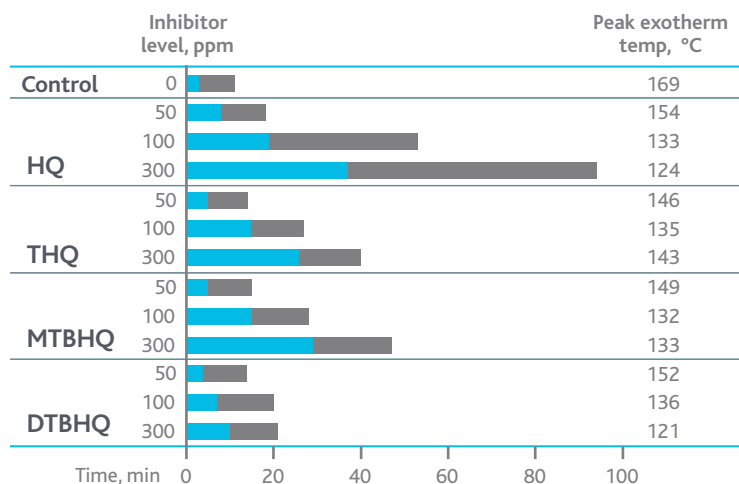
**Legend:** Gel time Propagation time\*



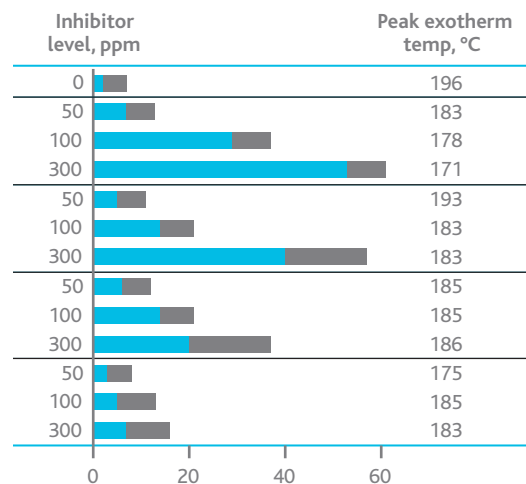
\*Propagation time = time from gelation to peak exotherm temperature.

## Room-temperature cure with BPO

**Figure 4** (PG/PA/MA 1:1.5) at various inhibitor levels<sup>a</sup>  
Initiated with 1 wt % benzoyl peroxide  
Promoted with 0.5 wt % dimethyl aniline



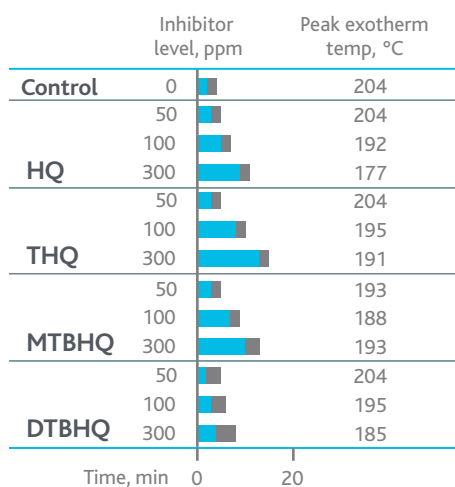
**Figure 5** (PG/PA/MA 1:3) at various inhibitor levels<sup>a</sup>  
Initiated with 1 wt % benzoyl peroxide  
Promoted with 0.5 wt % dimethyl aniline



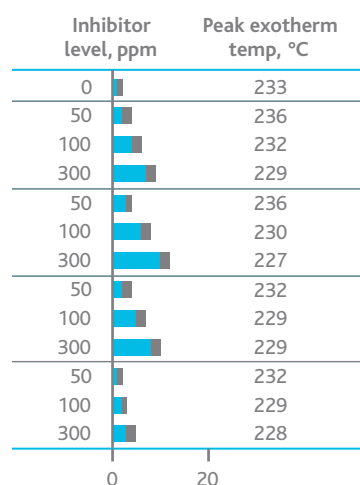
## Elevated-temperature cure with BPO

SPI exotherm test @ 82°C (180°F)

**Figure 6** (PG/PA/MA 1:1.5) at various inhibitor levels<sup>a</sup>  
Initiated with 1 wt % benzoyl peroxide



**Figure 7** (PG/PA/MA 1:3) at various inhibitor levels<sup>a</sup>  
Initiated with 1 wt % benzoyl peroxide



<sup>a</sup>PG = propylene glycol. PA = phthalic anhydride. MA = maleic anhydride.

Legend: Gel time Propagation time\*




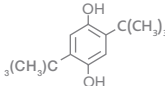
\*Propagation time = time from gelation to peak exotherm temperature.

For inhibitor levels evaluated at elevated temperature and for 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.

## Properties

**Table 1** Typical properties of Eastman™ hydroquinone and derivatives <sup>a,b</sup>

				
	HQ <sup>c</sup>	THQ	MTBHQ	DTBHQ
Empirical formula	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	C <sub>10</sub> H <sub>14</sub> O <sub>2</sub>	C <sub>14</sub> H <sub>22</sub> O <sub>2</sub>
Molecular weight	110.11	124.13	166.21	222.31
Physical form	crystals	crystals	crystals	crystals
Color	white to light tan	white to 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 <sup>d</sup> , °C	177	172	171	216
Fire point, °C	191	177	174	216
Autoignition temp., °C	499	452	457	421

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

<sup>b</sup>Typical property bulletins are available for all grades of hydroquinone and derivatives.

<sup>c</sup>Eastman offers 2 grades of hydroquinone: USP and photographic.

<sup>d</sup>Cleveland open cup.

**Table 2** Approximate solubility in vinyl monomers and various solvents <sup>a,b</sup>

	HQ <sup>c</sup>	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

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

<sup>b</sup>Inhibitor added in increments of 1 wt% and evaluated for solubility after 24 hours at ambient temperature.

<sup>c</sup>Eastman offers 2 grades of hydroquinone: USP and photographic.

Additional information on cure control is available in  
Eastman publication GN-396,  
*Eastman™ Copromoters for Effective Polyester Cure.*

For additional information on hydroquinone, see  
Eastman publication D-104,  
*Hydroquinone, Photographic Grade.*



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