EASTMAN

Corrosion-resistant polyester resins

Based on Eastman TMPD™ glycol

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In the corrosion-resistant equipment industry, products are engineered to withstand the attack of extremely harsh environmental products such as sulfuric acid, hydrochloric acid, caustic soda and hypochlorite solutions. Use of unsaturated polyester resins to manufacture storage tanks, process tanks, treatment facilities, pipes and scrubbers continues to grow as new infrastructure demands in Brazil, Russia, India and China (BRIC) accelerate. In addition to new installations, strong growth in developed countries is being driven by infrastructure reclamation projects and increased environmental regulations that require more effective scrubbers and treatment facilities. In many of these applications, corrosion-resistant, unsaturated, polyester resins prevail without the degradation usually seen in products manufactured from metals, such as steel and aluminum.

This market consists of both relatively low-cost, general-purpose, corrosion-resistant resins produced from propylene glycol (PG), isophthalic acid (PIA) and maleic anhydride (MA); and premium-quality resins based primarily on either bisphenol A (BIS A), vinyl ester (VE) or halogenated (HAL) unsaturated polyester (Eastman NPG™ glycol/chlorendic anhydride/MA) formulations.

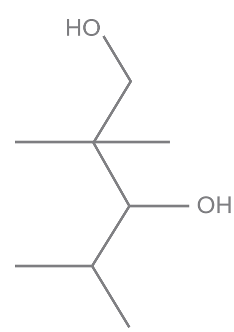
Unsaturated polyester resins based on Eastman TMPD™ glycol provide superior corrosion resistance in comparison to general-purpose resins and have other performance advantages that are useful in the fabrication of corrosion-resistant products. In addition, TMPD glycol-based polyesters are more economical than premium-quality formulations while providing comparable performance.

The branched, asymmetrical structure of Eastman TMPD™ glycol permits the preparation of noncrystalline polyesters. A sterically hindered, secondary hydroxyl group and the hydrophobic nature of this glycol combine to contribute outstanding performance and resistance to acids, alkali and other corrosive environments.

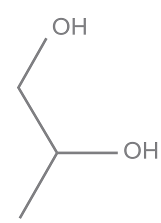
The bulky molecular structure of Eastman TMPD™ glycol prevents the close packing of resin molecules, imparting lower density to unsaturated polyester resins in comparison with PG-based formulations. This allows production of more molded parts for a given unit weight of resin. Additionally, less dense resins reduce the weight of the molded part possibly reducing expensive transportation cost. Molecular bulkiness also contributes to lower solution viscosity in styrene. This translates to better wetting of reinforcement fibers and better flow of resin solution with infusion-based manufacturing techniques. Lower solution viscosity also allows less styrene use, if desired, since application characteristics can be maintained at higher resin content. These attributes make using TMPD glycol in corrosion resins a strong value proposition for today's demanding customers.

The highly hindered, secondary hydroxyl group of Eastman TMPD™ glycol does react more slowly during resin synthesis than do primary or less-hindered, secondary hydroxyl groups. As a result, special synthetic considerations are required to produce resins that provide the stated performance levels. Eastman suggests the use of a synthesis catalyst to facilitate the preparation of TMPD glycol-based corrosion resins.

Laboratory evaluations have demonstrated many advantages of Eastman TMPD™ glycol in corrosion-resistant applications. However, optimum resin processability and subsequent cure characteristics are better achieved by incorporating a small amount of PG rather than using TMPD glycol as the sole glycol component. Fumaric acid (FA) can be substituted for MA to provide more fumarate isomer. Additionally, proper component staging is critical for optimum resin performance. Eastman studies have demonstrated incorporating PG in the second stage with either MA or FA enhances cure characteristics and cure consistency in TMPD glycol based corrosion resins.



Eastman TMPD™ Glycol



Propylene Glycol

Resin preparation, physical properties and cure

Table 1 Composition and physical properties of laboratory-prepared unsaturated polyesters

Physical properties	TMPD™ glycol/PIA[a]//PG/FA[b]	PG/PIA[a]//FA
Eastman TMPD™ glycol/PG molar ratio	75:25	—
Glycol excess, mole %	10	0.8
Acid molar ratio, sat:unsat acids	1:1	1:1
Fumaric content, wt %[c]	20.5	26.6
Fumarate isomer content, %[d]	99	99
Acid number	14	28
Molecular weight, M_n	2835	2550
Polydispersity, M_n/M_w	2.8	4.0
Resin T_g, °C (2nd heat)	44	49.5
ICI viscosity, neat resin @ 200° C, poise	9.4	8.4
Viscosity, 55 wt % in styrene, cP	228	540
APHA color	255	400
Density, 55 wt % in styrene, lb/gal	8.57	9.02
Typical reaction time, hours	15	16
Catalyst, butylstannoic acid, wt %	0.1	0.1

[a]*Manufactured by Eastman Chemical Company*

[b]*Double slash indicates staged reactants. Additionally, maleic anhydride can be substituted for fumaric acid with minor resin corrections.*

[c]*Weight percent fumaric varies slightly due to the higher molecular weight of TMPD™ glycol (146.22) compared to propylene glycol (76.10). Wt % fumaric acid content would be roughly equivalent at a 1:1.6 sat acid:unsat acid ratio for the Eastman TMPD™ glycol resin.*

[d]*Determined via NMR.*

New resin synthesis procedure using Eastman TMPD™ glycol

1. Purge with nitrogen and charge Eastman TMPD™ glycol to a reactor equipped with a heating mantle, agitator, partial condenser, temperature probe, water trap and total condenser. Refer to Eastman publication N-345.
2. Allow TMPD glycol to melt at 100° C taking care not to overheat reactor vessel sides. After melting, add isophthalic acid slowly to maintain slurry. Add catalyst at this point as well.
3. Under good agitation, increase temperature to 150° C at 1° C per minute followed by a ramp from 150° C to 200° C at 0.5° C per minute. Process the first stage at 200° C until an acid number of 8–10 is reached.
4. Cool the first stage prepolymer to 140° C and add propylene glycol. Allow temperature to recover and add fumaric acid (or maleic anhydride) slowly to the reactor.
5. Reheat to 200° C at 1° C per minute and process to an acid number of 10–15.

(Procedure for the all propylene glycol resin is similar except the first stage is PG, isophthalic acid and catalyst.)

Notes on curing

A copromoter should always be used for room-temperature curing of resins based on Eastman TMPD™ glycol. DMA (N, N-dimethylaniline) and DMAA (N, N-dimethylacetoacetamide) have been found to be effective copromoters when used with cobalt promoters (refer to Eastman publications GN-396, N-315 and N-317). It is important to note the cure window for maximizing physical properties of TMPD glycol-based corrosion resins is narrower than for PG based resins. However, the resin synthesis procedure on page 2 incorporates up-to-date procedure for optimum TMPD glycol-based resins. The procedure shows adding PG in the second stage with the unsaturated diacid. This change has been shown to significantly improve cure response and cure consistency with TMPD™ glycol-based resins versus adding the unsaturated diacid alone in the second stage. These results are depicted in Table 2. It should also be noted the fumaric acid level of the TMPD glycol resin is less than that of the PG control per Table 1.

Additional cure systems developed for TMPD™ glycol-based corrosion resins are shown in Table 3. Cure package A was used for Table 2 comparison.

Table 2 Cure comparison of old and new Eastman TMPD™ glycol synthesis technique

Cure property[a]	Old synthesis procedure	New synthesis procedure	PG control resin
Gel time, minutes	6.6	1.9	0.83
Peak exotherm temperature, °F	373	396	435
Time to peak exotherm, minutes	19	8	4
Barcol hardness development, 2 hr	<10	87	90
Barcol hardness development, 24 hr	76	90	90

[a]*Cured using the following cure system:*

Table 3 Room temperature cure systems for Eastman TMPD™ glycol-based corrosion resins

Promoters, wt %[a]	Cure package A	Cure package B	Cure package C	Cure package D
Cobalt octoate (6% Co)	0.4	0.5	0.5	0.5
Copromoters, wt %				
Eastman™ DMAA	0.3	0.3	—	—
DMA	—	—	0.3	0.3
Catalyst, wt %				
MEKP	1.0	1.0	1.0	1.5
Inhibitors, ppm				
Eastman™ hydroquinone (HQ)	100	100	150	150
Eastman™ mono-t-butylhydroquinone (MTBHQ)	—	200	150	150

[a]*Based on total resin weight*

Field testing pipes

Fiberglass-reinforced pipe samples were prepared by a fabricator of commercial equipment using the experimental Eastman TMPD™ glycol/PG/PIA//MA resin, a commercial PG/PIA//MA and a commercial BIS A resin. The pipe samples were installed in a feed line from a chemical manufacturing process to a waste treatment facility at Eastman.

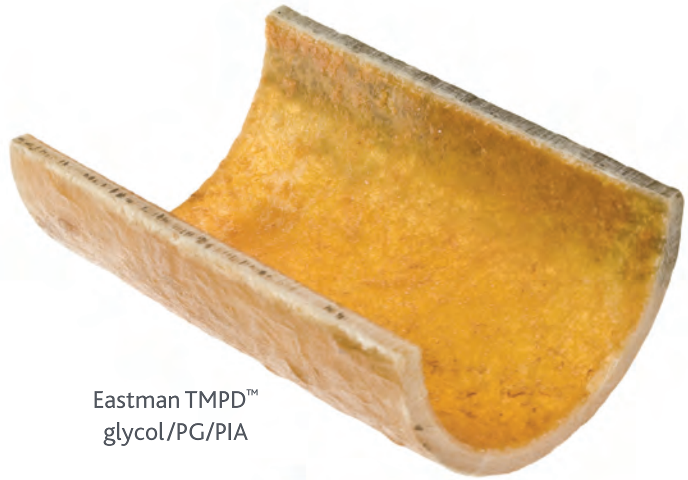
The feed line provided an extremely severe environment for testing. The line carried a strong aqueous solution of sulfuric and hydrochloric acids containing small amounts of low molecular weight organic solvents, dissolved gases such as sulfur dioxide, and acid salts at temperatures varying from 32° to 93°C (148° to 200°F). This environment would be considered too corrosive for metal pipes.

After 6 months exposure, the pipe sections were removed and examined. The results indicated the formulation based on Eastman TMPD™ glycol provided better performance than formulations based on either the general-purpose or the premium-quality corrosion-resistant resin.

These in-service test results agree with laboratory data on unreinforced castings that unsaturated polyester resins based on Eastman TMPD™ glycol/PG/PIA//MA provide better performance than commonly used corrosion-resistant resins.

Pipe samples

(6 months exposure)



Eastman TMPD™ glycol/PG/PIA

PG/PIA

Bisphenol A

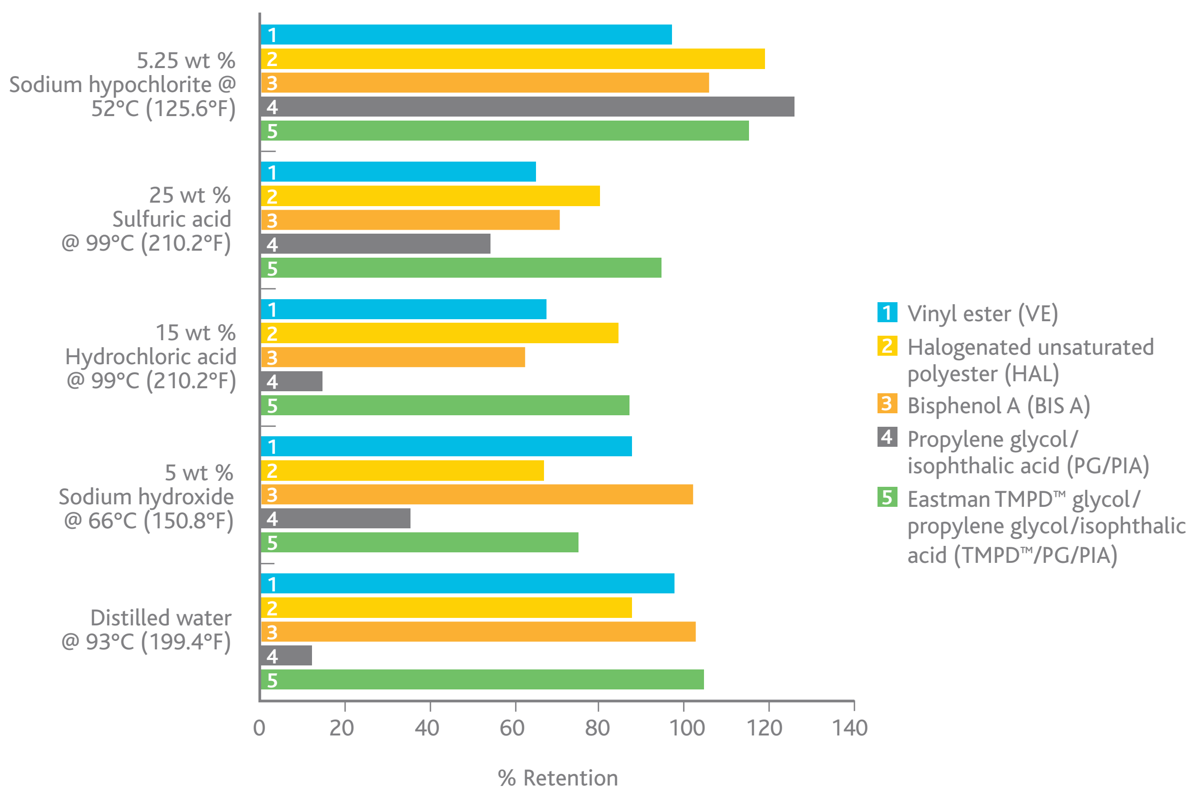
Testing castings

The corrosion resistance of unreinforced castings was evaluated by determining the percentage of original flexural strength retained after accelerated aging in various chemical environments for specified test intervals.

The castings were prepared in the laboratory to 1/8-inch thickness and cured for 3 hours at 70°C (158°F), 1 hour at 100°C (212°F) and 1 hour at 150°C (302°F) using 0.5% benzoyl peroxide as a catalyst. **Note: Elevated temperature cures generally do not require the use of copromoters.**

The overall corrosion resistance of the castings is shown in Figure 1. The castings prepared with resins based on Eastman TMPD™ glycol were found to have excellent resistance to corrosive environments. These samples provided better flexural strength retention than samples prepared with the PG/PIA//MA resin in most environments tested. The TMPD glycol/PG/PIA//MA resin exhibited favorable strength retention when compared with the commercial formulations as well.

Figure 1 Flexural strength retention of castings
(6 months exposure)



Summary

Data from this study demonstrates that resins based on Eastman TMPD™ glycol offer excellent corrosion resistance properties that exceed the performance of both low-cost, general-purpose, corrosion-resistant resins and of more expensive, premium-quality resins in many chemical environments. High performance and low cost makes TMPD glycol an attractive choice for manufacturers and fabricators of corrosion-resistant, polyester-based composites.

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