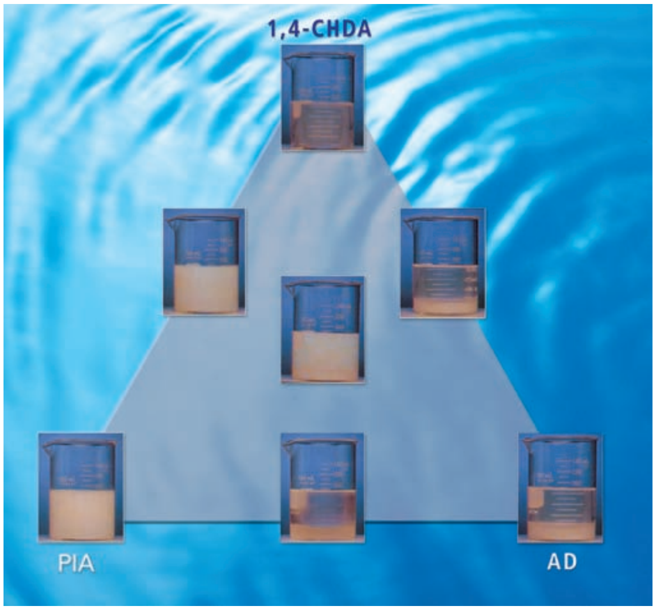
Improved hydrolytic stability of waterborne polyester resins with Eastman™ 1,4-CHDA and Eastman TMPD™ glycol



Introduction

Waterborne coatings provide a viable means of complying with VOC (volatile organic compound) requirements. An inherent problem with amine-neutralized waterborne polyester resins is their hydrolytic instability due to hydrolysis of the ester linkages in the pH range of 8–9. This hydrolysis reduces the molecular weight of the resin, leading to poor coatings performance and/or precipitation of the resin from the dispersion. Storage temperature, pH, degree of neutralization, hydrophobicity, polar (inductive) effects, steric factors, and anchimeric effects are all thought to be important variables that control the rate of ester hydrolysis. Several of these variables can be controlled by monomer selection.

Eastman 1,4-CHDA (1,4-cyclohexanedicarboxylic acid) and Eastman TMPD™ glycol (2,2,4-trimethyl-1,3-pentanediol) have been shown to have numerous benefits in resins for solution coatings[1] as listed in the following.

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[1] *See Eastman publication N-329 (Eastman triangle glycol study).*

Benefits of Eastman™ 1,4-CHDA based coatings

Coatings performance

- Hardness/flexibility balance
- Chemical, corrosion, detergent, and stain resistance
- Rapid reactivity

Resin processing

- Low resin color
- Excellent solubility in common glycols

Benefits of Eastman TMPD™ glycol based coatings

Coatings performance

- Lower viscosity (VOC)
- Chemical resistance
- Excellent solubility

Resin processing

- Rapid reactivity
- Low resin color
- Low melting point

This study shows that 1,4-CHDA and TMPD glycol also offer improved hydrolytic stability for polyester resin dispersions compared with other common diacids and glycols. The superior stability of the ester bonds derived from TMPD glycol and Eastman 1,4-CHDA makes these intermediates the monomers of choice for waterborne polyester resins.

Experimental—diacid study

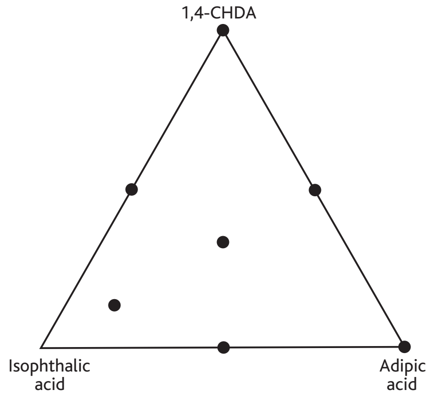
Diacids studied

Eastman™ 1,4-CHDA was compared to Eastman™ purified isophthalic acid (PIA) and adipic acid (AD) for hydrolytic stability. Eastman™ PIA and AD are widely used in combination with each other to make saturated polyesters for coatings applications. PIA, being an aromatic diacid, has the highest dissociation constants, K_a (lowest pK_a) of the diacids studied, indicating that it should have the least resistance to base-catalyzed hydrolysis. PIA is also the most hydrophobic of the diacids. AD is the most soluble of the three in water, but it has much lower dissociation constants. Eastman™ 1,4-CHDA has a cycloaliphatic structure that allows for better steric shielding than AD as well as low dissociation constants. It is also much more hydrophobic than AD.

Experimental design

The diacids were evaluated using a statistically designed mixture study. The resin compositions are represented as dots on Figure 1. Each apex of the triangle indicates 100 weight % usage of the diacid in that resin composition. The midpoint of each leg represents a 1:1 molar blend of two diacids, and the center point is a resin composition that contains an equimolar blend of all three diacids. Attempts to make a 100 weight % PIA resin were unsuccessful due to incomplete reaction; therefore, a blend of PIA/1,4-CHDA/AD (75/12.5/12.5) was substituted.

Figure 1
Experimental design



Synthesis

Five resins were prepared for each dot on the triangle using a waterborne resin formulation based on Eastman TMPD™ glycol. All resins were prepared with the same diacid/glycol equivalent ratio and the same Eastman™ 1,4-CHDA/TMA ratio as shown in Table 5. Variation in glycol molecular weight resulted in some variation in resin molecular weight, acid number, and hydroxyl number. Resin compositions and properties are shown in Table 1. The resins were prepared as catalyzed two-stage cooks with the least reactive diacid being in the first stage. Resins containing only one diacid were single-staged.

Table 1 Resin composition and properties

Resin composition	
Eastman TMPD™ glycol/trimethylolpropane/diacid intermediates	
Molar ratio: 8.7/2.8/11.6	
Fascat™ 4102 catalyst:[a] 0.1% of resin charge	
Resin properties	
Final acid number, mg KOH/g resin	48–52
Molecular weight (M_n, number average), calculated	1,800–2,200
Hydroxyl number, mg KOH/g resin, calculated	80–100
Weight % solids in solvent blend[b]	75

[a] *Atofina Chemicals*

[b] *Eastman™ EB/Eastman™ DE glycol ethers at 90/10 weight % ratio*

Dispersion preparation and stability testing

The dispersions were prepared according to the formulation in Table 2. Stability studies were carried out on the dispersions both at ambient temperatures (ca. 23°C [73°F]) and at 52°C (126°F). Changes in M_w (weight average), dispersion appearance, and pH were monitored.

Table 2 Typical dispersion composition

Ingredients	Weight, g
Polyester resin (75% N.V.)	36.6
2-dimethylaminoethanol[a]	2.6
Water (deionized)	60.8
	100.0

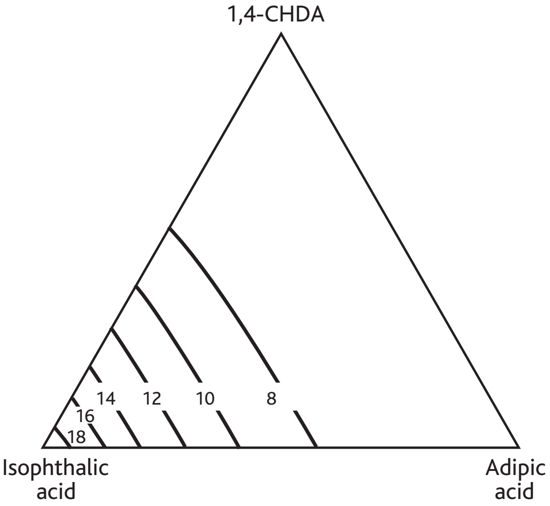
[a] *Resulted in a pH range of 8.7–9.1*

Results—diacid study

Resin processability

Cook times were shorter for resins containing Eastman™ 1,4-CHDA than for those containing Eastman™ PIA and AD (Figure 2). While AD has the fastest reaction rate, it required a lower reaction temperature to minimize foaming.

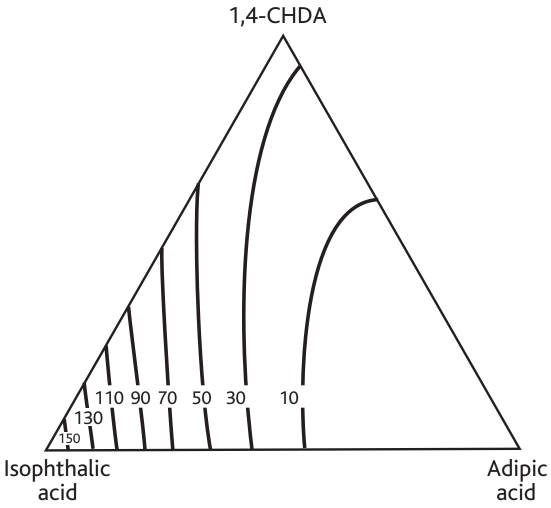
Figure 2
Cook times (hours)



Resin solution viscosity

At 75 weight % solids, the major contributor to solution viscosity is Eastman™ PIA (Figure 3).

Figure 3
Resin solution viscosity (Pa·s) at 75 weight % solids in cosolvent



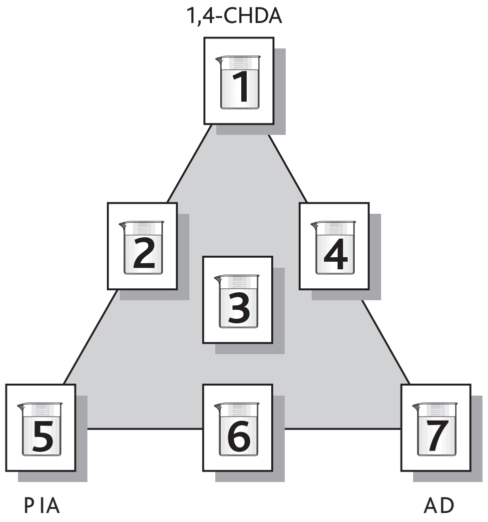
Resin dispersion stability—appearance

The least change in appearance, which can be viewed as one indication of dispersion stability, was achieved as the Eastman™ 1,4-CHDA content was increased. All dispersions were initially clear and homogeneous. Dispersion clarity after 13 weeks at 52°C (126°F) is illustrated in the cover photograph. Resin dispersions shown in the photograph are identified in Table 3.

Table 3 **Resin dispersions after 13 weeks at 52°C (126°F)**

Dispersion[a]	1,4-CHDA	PIA	AD	Appearance
1	100	0	0	Clear
2	50	50	0	Hazy
3	33	33	33	Hazy
4	50	0	50	Separated
5	12	75	12	Hazy
6	0	50	50	Separated
7	0	0	100	Separated

[a] *See the following key.*



Resin dispersion stability—pH

Change in dispersion pH occurs when polyester resins are hydrolyzed. The pH change in dispersions containing Eastman™ 1,4-CHDA was less than with Eastman™ PIA- and AD-containing systems (Figures 4 and 5). The higher the level of 1,4-CHDA in the system, the lower the change in pH.

Figure 4

Percent reduction in pH after 13 weeks at 52°C (126°F)

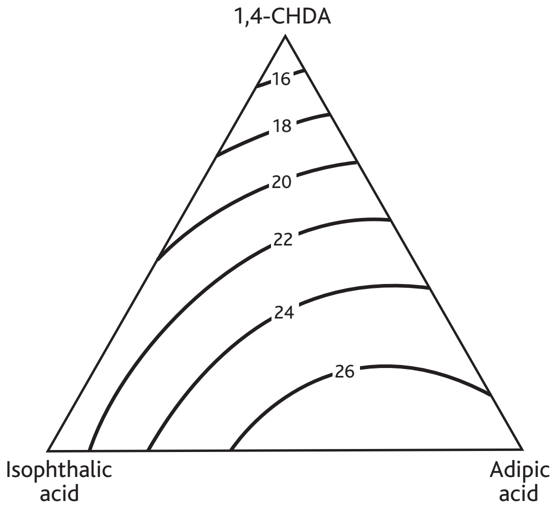
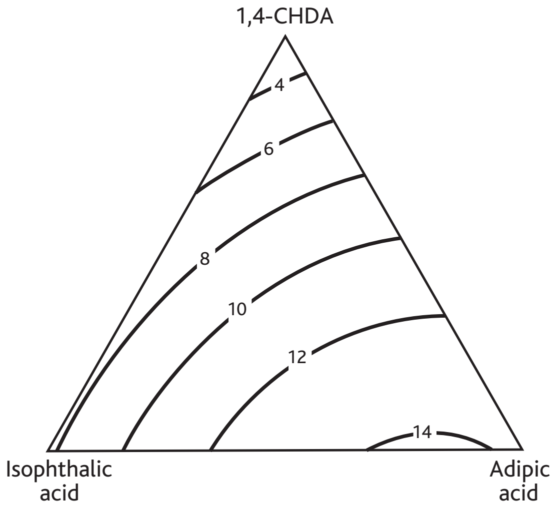


Figure 5

Percent reduction in pH after 12 months at ambient temperature



Resin dispersion stability—molecular weight

Hydrolysis of a polyester resin results in cleavage of the polymer chain and a corresponding decrease in molecular weight (M_w, weight average). The resin dispersions containing 1,4-CHDA showed less decrease in M_w than those containing PIA and/or AD—the more 1,4-CHDA used, the less change in M_w (Figures 6 and 7).

Figure 6
Percent reduction in Mw after 4 weeks at 52°C (126°F)

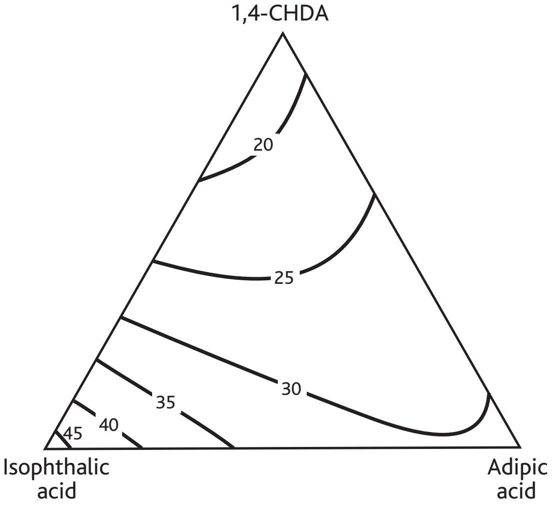
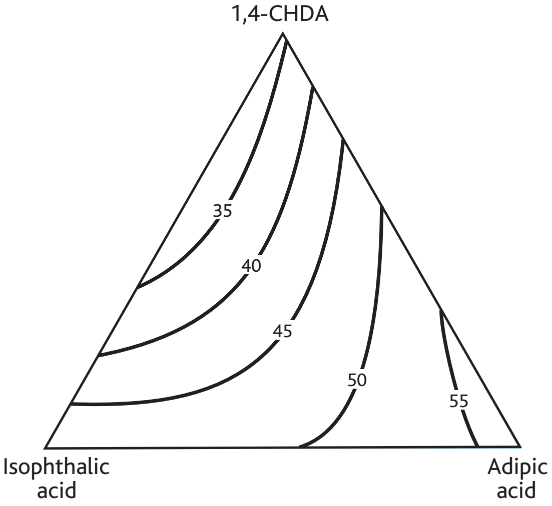


Figure 7
Percent reduction in M_w after 13 weeks at 52°C (126°F)



Conclusion—diacid study

- 1,4-CHDA and AD had the best processability and the lowest solution viscosity. PIA ranked third.
- 1,4-CHDA imparted the best dispersion stability, followed by PIA, and finally AD.
- 1,4-CHDA offers good processability, low viscosity, and excellent waterborne dispersion stability, in addition to the unique balance of hardness and flexibility as previously demonstrated in solution coatings.[1]
- 1,4-CHDA would make ideal polyester dispersion for modifying acrylic dispersion and still maintain acceptable storage stability.

Table 4 **Effect of diacids on waterborne polyester resins and dispersions**[a]

		1,4-CHDA	PIA	AD
Resin properties	Processability	1	3	1
	Solution viscosity	2	3	1
Dispersion stability	Appearance	1	2	3
	pH	1	2	3
	M_w	1	2	3

[a] *1 = best; 3 = worst*

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[1] *See Eastman publication N-335 (A statistical comparison of Eastman™ 1,4-CHDA, Eastman™ PIA, AD, and HHPA in a high-solids resin system based on Eastman TMPD™ glycol).*

Experimental—glycol study

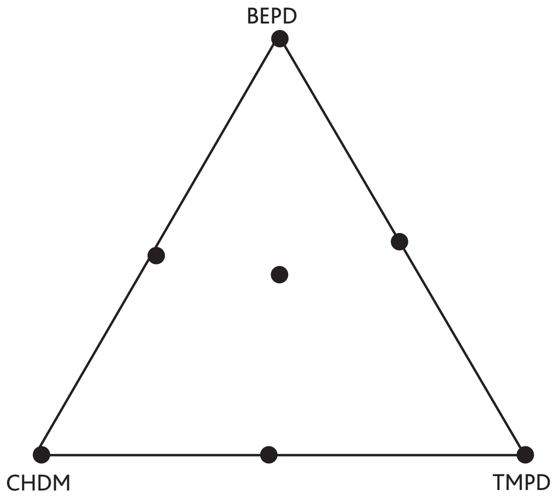
Glycols studied

In the present study, three glycols are evaluated for their effects on the hydrolytic stability of Eastman™ 1,4-CHDA-based amine-neutralized waterborne polyester resins. The effects of glycol structure were determined for Eastman TMPD™ glycol, Eastman™ 1,4-CHDM, and BEPD glycol (2-butyl-2-ethyl-1,3-propanediol).

Experimental design

Glycol effects on the hydrolytic stability of polyester dispersions were evaluated utilizing a statistically designed three-component mixture experiment. The apices of the triangle represent 100 mole % of that glycol in the resin, while each midpoint represents a 1:1 molar blend of the two glycols on that leg of the triangle. The center point represents an equimolar blend of the three glycols and is duplicated for statistical analysis (Figure 8).

Figure 8
Experimental design



Resin synthesis

All resins were made with the same diacid/glycol equivalents ratio keeping the diacid (1,4-CHDA/TMA) constant and synthesized to the same extent of reaction. Variation in glycol molecular weight resulted in some variation in resin molecular weight, acid number, and hydroxyl number. The superior hydrolytic stability of polyester resins based on Eastman™ 1,4-cyclohexanedicarboxylic acid makes it the diacid of choice in designing resin formulations for evaluation of glycol effects on hydrolytic stability. Resin composition and properties are shown in Table 5.

The polyester resins were synthesized using two-stage reactions with the glycols and trimellitic anhydride charged to the first stage. For resins containing TMPD glycol, it is important to charge the trimellitic anhydride to the molten glycol rather than melting both simultaneously. This substantially reduces color formation and glycol decomposition. The first-stage reaction mixture was maintained at 180°C (356°F) until acid number analysis indicated the first two carboxyl groups of the TMA were esterified. The 1,4-CHDA was then charged to the mixture, and the second-stage reaction was maintained at 180°C (356°F) until the desired acid number was reached. Incorporating the TMA in the backbone of the resin molecules, rather than at the ends, and processing the resins to the same extent of reaction resulted in identical resins except for the glycol moieties in the backbone. These processing techniques allowed isolation of the effect of glycol structure on the hydrolytic stability of the resins.

Table 5 Composition and properties

Resin composition	
Glycol intermediates/Eastman™ 1,4-CHDA[a]/TMA[b]	
Equiv. ratios: 1.06:0.63:0.37	
Resin properties	
R value	1.06
Functionality, f_{OH}	2
Extent of reaction, Pa	0.87
M_n, molecular weight range[c]	1,382–1,468
Acid number range,[c] mg KOH/g resin	50–53
Maximum reaction temperature, °C (°F)	180 (356)
Weight % solids in Eastman™ EB	80

[a] *1,4-cyclohexanedicarboxylic acid charged to second stage of two-stage reaction.*

[b] *Trimellitic anhydride charged to first stage with 100 mole % of glycol intermediates.*

[c] *Ranges reported because of differences in glycol molecular weight.*

Dispersion preparation

Resin dispersions were prepared according to the formulation in Table 6. A 100 weight % neutralization of the polyester was achieved by addition of 2-dimethylaminoethanol according to the equation:

$$\text{Wt amine, g} = \frac{(\text{wt resin, g}) \times (\text{acid number}) \times (\text{amine } M_w)}{56{,}100}$$

Table 6 Resin dispersion formulation

Component	Wt%
Polyester resin (neat)	35.0
Eastman™ EB	8.8
Deionized water	56.2
2-Dimethylaminoethanol[a]	Calculated

[a] *Resulted in pH range of 8.6–9.0*

Enamel formulation

Pigmented enamels were prepared from each resin according to the formulation in Table 7. Enamels were prepared immediately after dispersion of the resins in water and after aging the dispersions at 52°C (126°F) for 4 weeks. The enamels were adjusted to a #4 Ford cup viscosity of 30 seconds and sprayed onto unprimed, Bonderite™ 1000 pretreated, cold-rolled steel test panels. The enamels were then cured for 30 minutes at 163°C (325°F).

Table 7 Enamel composition

Ingredient	Wt%
Masterbatch	
Cymel™ 303 melamine resin[a]	16.8
Ti-Pure™ R-900 TiO_2 pigment[b]	48.9
Fluorad™ FC-430[c]	3.3
Disperbyk™ 181[d]	0.1
Eastman™ EB	2.1
Deionized water	28.2
Coating (200 g)	
Masterbatch	65 (g)
Dispersed resin (35% solids)	135 (g)

[a] *Cytec*

[b] *DuPont*

[c] *3M*

[d] *BYK Chemie*

Results—glycol study

Stability testing

A portion of each resin dispersion was subjected to accelerated aging at 52°C (126°F) for 4 weeks. The dispersions were checked weekly for pH drift and increase in acid number. Pigmented enamels from each resin dispersion were prepared initially and at the end of 4 weeks. In addition, a portion of each resin dispersion was aged under ambient conditions for 1 year. Acid number and pH were monitored once every 3 months. The responses from both sets of aged dispersions were then plotted as percent acid number increase, percent pH decrease. Changes in enamel properties were plotted as percent increase in MEK double rubs.

Resin dispersion stability—4 weeks accelerated aging

The relative stabilities of the resin dispersions were determined by monitoring the increase in acid number and the decrease in pH. Both responses are directly proportional to the amount of hydrolysis of the polyester chains that occurred during aging. The percent increase in acid number of the dispersions after accelerated aging for 4 weeks at 52°C is shown in Figure 9. The pH responses are plotted in Figure 10.

The data shows that Eastman TMPD™ glycol imparts superior hydrolytic stability to the resin dispersions. The resin containing 100 mole % TMPD glycol was clearly the most stable to hydrolysis, and the data shows a direct correlation between hydrolytic stability and TMPD glycol content in any given resin formulation. Thus, TMPD glycol can be blended with other glycols to improve the hydrolytic stability of a given resin formulation.

Figure 9

Eastman™ 1,4-CHDA/TMA/glycol dispersions (Percent increase in acid number after 4 weeks @ 52°C [126°F])

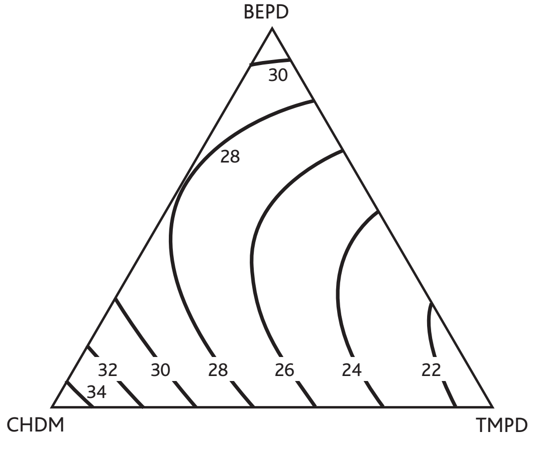
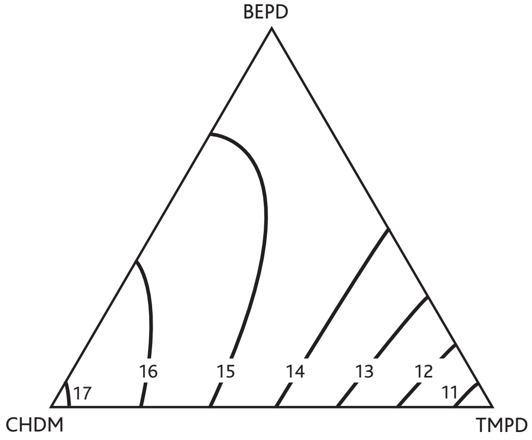


Figure 10

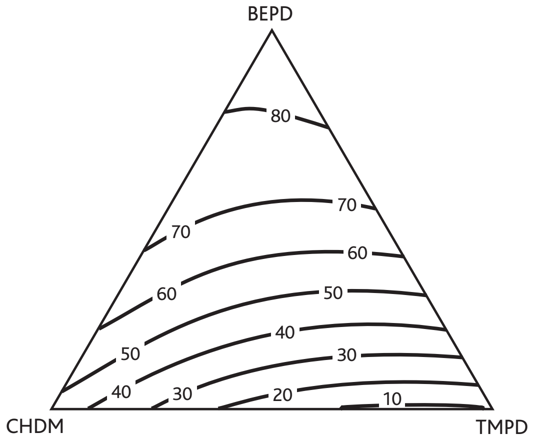
Eastman™ 1,4-CHDA/TMA/glycol dispersions (Percent reduction in pH after 4 weeks @ 52°C [126°F])



Enamel properties

Polyester chain hydrolysis results in an increase in both hydroxyl and carboxyl functional groups and should result in a higher cross-link density for the corresponding melamine cross-linked films. Thus, there should be a correlation between the amount of resin hydrolysis and film hardness. To confirm this, the resin dispersions subjected to accelerated aging were formulated into pigmented enamels at the end of 4 weeks according to the formulation in Table 6. The percent increase in MEK (methyl ethyl ketone) double rubs was determined and is shown in Figure 11. These results correlate well with the acid number and pH results, with the cured enamels prepared from resins based on Eastman TMPD™ glycol exhibiting the smallest increase in MEK double-rub resistance.

Figure 11
Changes in enamel properties (percent increase in MEK double rubs after 4 weeks @ 52°C [126°F])



Resin dispersion stability—12 months ambient aging

A portion of each dispersion was aged at ambient conditions for 12 months. Acid number and pH measurements were taken every 3 months during this time. The percent acid number increase (Figure 12) and the percent pH decrease (Figure 13) correlated well with the accelerated aging results. Again, resins containing increasing amounts of Eastman TMPD™ glycol exhibit increasing resistance to hydrolysis with the resin containing 100 mole % TMPD glycol giving the best performance.

Figure 12
Percent increase in acid number (12 months ambient conditions)

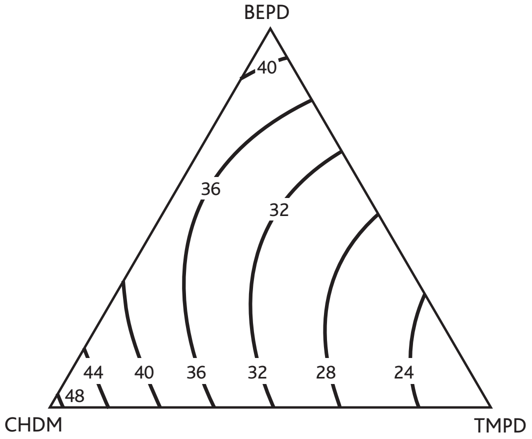
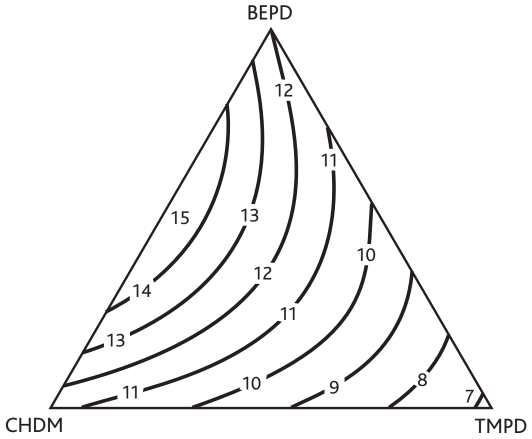


Figure 13
Percent reduction in pH (12 months ambient conditions)



Conclusion—glycol study

- Eastman TMPD is the glycol of choice for formulating waterborne polyester resins. The hydrophobicity, because of its bulky asymmetrical structure and the sterically shielded secondary hydroxyl group, results in ester linkages that are extremely resistant to hydrolysis. TMPD can also be used as a modifying glycol to improve the hydrolytic stability of polyester resins based on other glycol intermediates.
- The combination of Eastman™ 1,4-CHDA and Eastman TMPD™ glycol is an excellent choice for hydrolytically stable polyester resins and polyester polyols for waterborne polyurethanes.

Summary

Proper selection of resin intermediates can minimize the tendency of polyester resins to undergo hydrolysis. When formulated into typical waterborne coatings, Eastman™ 1,4-CHDA-based polyesters will resist hydrolysis much better than Eastman™ PIA- and/or AD-based resins. 1,4-CHDA and Eastman TMPD™ glycol can be used alone or in combination to make polyesters that are much more hydrolytically stable than current systems.

Eastman™ 1,4-CHDA and Eastman TMPD™ glycol were shown to provide the following benefits to waterborne resins:

Benefits of Eastman™ 1,4-CHDA

- Excellent resin stability in water
- Better reactivity than PIA during resin synthesis
- Lower resin viscosity in cosolvent compared with PIA

Benefits of Eastman TMPD™ gycol

- Excellent resin stability in water
- Lower resin viscosity in cosolvent

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