Statistical Study of Hydrolytic Stability in Amine-Neutralized Waterborne Polyester Resins as a Function of Monomer Composition

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Reversibility of the esterification reaction has limited the use of polyester resins in waterborne coating systems. As with other polyester resin properties, the rate of hydrolysis can be modified by choice of monomer. The objective of this study is to demonstrate changes in hydrolytic stability in waterborne polyesters as a function of change in glycol and diacid composition. In the glycol section of the study, BEPD and HPHP were compared. For the diacid section, adipic acid, isophthalic acid, and 1,4-CHDA were examined.

Aqueous dispersions were subjected to storage at both ambient and elevated temperature. Response factors measured over time included molecular weight, pH, appearance, and change in properties of coatings made from the aged dispersions. Results are discussed with reference to accepted hydrolysis rate theories. Results show that inductively stabilized, hydrophobic monomers such as 1,4-CHDA and BEPD produce the most stable waterborne polyesters of the glycols and diacids studied.

INTRODUCTION

The advantages of polyester resins in coatings applications are well-known. A wide variety of monomers allows the resin chemist to build polyester molecules with an excellent range of performance properties, and formulators have become skilled in using these properties to meet consumer needs.

Current legislation has driven coatings manufacturers to technologies that reduce volatile organic compound (VOC) emissions. Because of their range of properties, polyester resins have played a major role in the development of coating technologies that reduce VOC emissions. Examples such as coil and powder coatings are dominated by polyesters.[1] Polyesters also play a large role in high-solids coatings. Waterborne coatings are the major exception due to the reversibility of the esterification reaction in water.

It is known that various monomers provide differing degrees of hydrolytic stability to polyesters through structural differences. While many published studies have been done in the past to understand structure in relation to ester hydrolysis, apparently all have been studies of model esters rather than polymers.[2-5] Also, several newer monomers have been introduced in recent years that have never been studied. In this paper we will discuss two polyester resin studies that compare the newer resin intermediates to monomers commonly used in polyester resins for coatings applications.

EXPERIMENTAL

Diacid Study Design

A triangular mixture design experiment was chosen to compare 1,4-CHDA (1,4-cyclohexanedicarboxylic acid) with IPA (isophthalic acid) and AD (adipic acid). The study used a waterborne resin formulation which is based on TMPD glycol (2,2,4-trimethyl-1,3-pentanediol). The design of the experiment is shown in *Figure* 1 with a dot representing each resin included in the study. Each apex of the triangle indicates 100% usage of the diacid in that resin composition. The midpoint of each side represents a 1:1 molar blend of two diacids, and the center point is a resin composition containing an equimolar blend of all three diacids. Attempts to make

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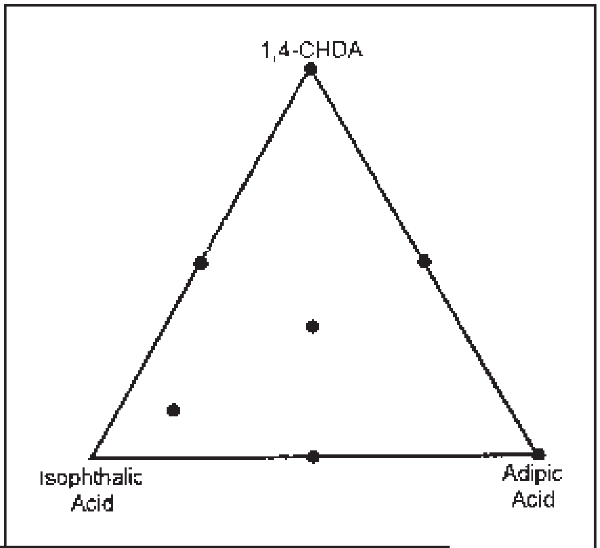

Figure 1—Experimental design.

a 100% IPA resin were unsuccessful due to incomplete reaction; therefore, a blend of IPA/1,4-CHDA/AD (6:1:1) was substituted.

Five resins were prepared for each formulation shown. Resin compositions and properties are shown in *Table* 1. A mole-for-mole replacement of one acid for another was used in the resin design. The resins were prepared as catalyzed two-stage reactions with the least reactive diacid in the first stage. Resins containing only one diacid were single staged (*Table* 2).

Preparation of Resin Dispersions

The resins were reduced to 75% solids in a blend of Eastman EB (ethylene glycol monobutyl ether) and Eastman DE (diethylene glycol monoethyl ether) solvents (9:1, respectively). The resins were then neutralized with 2.6 g of DMEA (2-dimethylethanolamine) and dispersed in water. This resulted in a pH range of 8.7 to 9.1 (*Table* 3).

Table 1—Resin Composition and Properties

Resin Composition

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	48-52
Molecular weight (M_n), calculated	1800-2000
Hydroxyl number, calculated	80-100
Percent solids in solvent blend[b]	75

(a) Elf Atochem.
(b) Eastman EB/Eastman DE glycol ethers at 90/10 ratio.

Stability Testing

The resin dispersions were aged at 52°C for 13 weeks and at room temperature for one year. Molecular weight, pH, and appearance were monitored.

Enamels prepared from dispersions that had been aged for seven weeks at 52°C (*Table* 4) were drawn down on zinc phosphate-treated steel test panels and cured at 177°C for 30 min. Physical properties of the cured enamels from the aged dispersions were compared with the physical properties of cured enamels prepared from unaged resin dispersions.

Resin dispersions were also checked for pH drift and molecular weight change after aging for four weeks at 52°C.

Glycol Study Design

NPG glycol (2,2-dimethyl-1,3-propanediol), BEPD (2-butyl-2-ethyl-1,3-propanediol), and HPHP (3-hydroxy-2,2-dimethylpropyl 3-hydroxy-2,2-dimethylpropanoate) were evaluated using a triangular mixture study.

The resin compositions are represented as dots in *Figure* 2. Each apex of the triangle indicates 100% usage of the glycol in that resin composition. The midpoint of each side represents a 1:1 molar blend of two glycols, and the center point is a resin composition that contains an equimolar blend of all three glycols. The center point is duplicated for statistical purposes providing a total of eight resins for the study.

A mole-for-mole replacement of one glycol for another was used in the resin design (*Table* 5). Also, the equivalents ratio between the acid components and the glycol(s) was kept constant. All the resins were synthesized to the same extent of reaction (degree of polymerization). By keeping molar ratios and extent of reaction constant, the resulting resins were identical except for the glycol moieties in the backbone. Because the glycols have differing molecular weights and resin functionality is kept constant, molecular weight, acid number, and hydroxyl number change with glycol composition. Target and analytically-determined resin properties are given in *Table* 6.

Preparation of Resin Dispersions

The resins were reduced to 80% solids in Eastman EB solvent and dispersed in water (*Table* 7). DMEA was used to neutralize the polyester resins to 100% based on acid number measurements using the following equation:

$$\text{Wt. amine} = \frac{(\text{Wt. resin}) \times (\text{resin A.N.}) \times (\text{amine M.W.})}{56{,}100}$$

Table 2—Staging of Acids in Resin Cooks

	CHDA/IPA/AD						
Stage	**100/0/0**	**50/50/0**	**0/50/50**	**50/0/50**	**0/0/100**	**$33^1/_3/33^1/_3/33^1/_3$**	**$12^1/_2/75/12^1/_2$**
1	CHDA	IPA	IPA	CHDA	AD	IPA	IPA
2	—	CHDA	AD	AD	—	CHDA/AD	CHDA/AD

Table 3—Typical Dispersion Formulation

Components	Wt %
Polyester resin (75% solids)	36.6
2-Dimethylaminoethanol[a]	2.6
Water (deionized)	60.8
	100.0

(a) Resulted in pH range of 8.7-9.1.

Table 4—Enamel Formulation

Components	Wt %
Resin dispersion (Table 3)	53.9
Tioxide RTC 4 TiO_2[a]	21.3
Cymel 303 melamine resin[b]	18.2
Water (deionized)	6.4
p-Toluenesulphonic acid[c]	0.2
	100.0

Pigment: Binder	50:50
Resin: Crosslinker	70:30

(a) Tioxide Group.
(b) Cytec.
(c) 40% in isopropyl alcohol.

Table 5—Resin Composition and Design

Resin Composition

Glycol intermediates/Eastman 1,4-CHDA-R[a]/TMA[b]
Equivalents ratio: 1.06/0.63/0.37
R value = 1.06

Resin Design

Extent of reaction[c], ρ_a	0.87
Hydroxyl functionality, f_{OH}	2
Acid functionality, f_{COOH}	1
Molecular weight range[d], M_n	1188-1658
Acid number range[d]	62-44
Hydroxyl number range[d]	92-68
Maximum reaction temperature, °C	180
Percent solids in Eastman EB solvent	80

(a) 1,4-Cyclohexanedicarboxylic acid (1,4-CHDA) charged to second stage of two-stage reaction.
(b) Trimellitic anhydride (TMA) charged to first stage with 100% of the glycol intermediates; TMA incorporated into the backbone.
(c) Same percentage of acid equivalents reacted into each resin.
(d) Ranges reported due to differences in glycol molecular weights creating differences in resin molecular weights, acid numbers, and hydroxyl numbers.

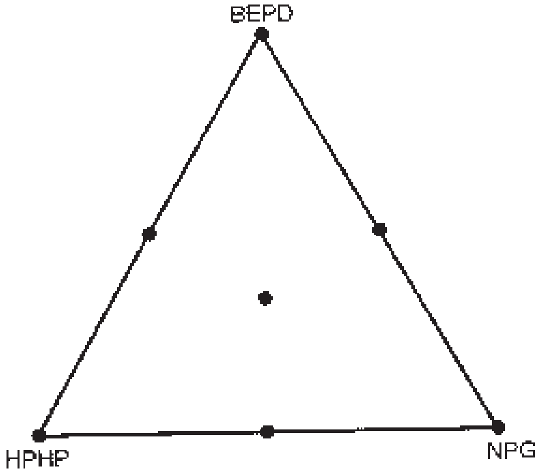

Figure 2—Experimental design.

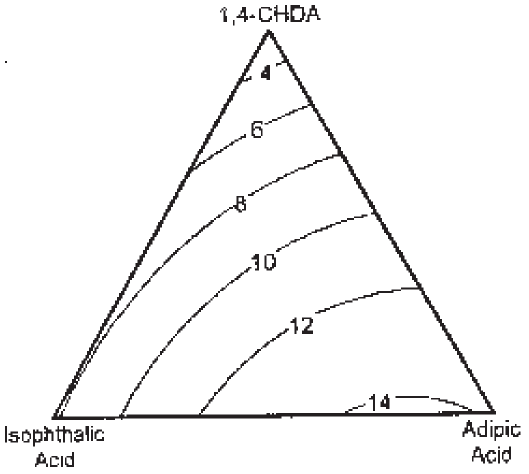

Figure 3—Percent reduction in pH after one year at room temperature.

Table 6—Resin Properties (Target vs Actual)

Glycol Composition BEPD/HPHP/NPG	Target M_n	Actual M_n[a]	Target AN	Actual AN[b]	Acutal ρ_a[c]
100/0/0	1468	1615	50	49.1	0.871
50/50/0	1599	1537	46	44.6	0.874
0/100/0	1658	1603	44	45.7	0.861
0/0/100	1188	1423	62	63.0	0.869
50/0/50	1308	1631	56	57.0	0.866
0/50/50	1404	1580	52	54.3	0.861
$33^1/_3/33^1/_3/33^1/_3$	1475	1627	50	50.8	0.869
$33^1/_3/33^1/_3/33^1/_3$	1475	1657	50	49.0	0.874

(a) Determined by gel permeation chromatography (GPC).
(b) ASTM D 1639-83.
(c) Extent of reaction.

Table 7—Resin Dispersion Formulation

Component	Wt %
Polyester resin (80% solids)	43.8
Water (distilled)	56.2
	100.0
2-Dimethylaminoethanol[a]	Calculated

(a) Resulted in pH range of 8.3-8.9.

Measurements indicated that pH ranged from 8.3 to 8.9 (*Table* 8).

Stability Testing

The resin dispersions were aged for one year at 23°C and then checked for pH drift and change in appearance.

A portion of each aged dispersion was formulated into enamels (*Table* 9). The enamels were sprayed onto unprimed, zinc phosphate-treated, cold-rolled steel test panels and cured for 30 min at 163°C. Physical properties of the cured enamels from the aged dispersions were compared with the physical properties of cured enamels formulated from the resin dispersions before aging.

Table 8—Dispersion Composition and pH

Glycol Composition BEPD/HPHP/NPG	Dispersion Composition (Wt %)				
	Resin NV_m	EB	Water	DMEA	pH
100/0/0	34.1	7.6	55.6	2.7	8.8
50/50/0	34.1	8.5	54.9	2.4	8.4
0/100/0	34.1	8.3	55.1	2.5	8.6
0/0/100	33.8	8.1	54.7	3.4	8.8
50/0/50	33.9	7.9	55.1	3.1	8.9
0/50/50	34.0	7.9	55.2	2.9	8.5
$33^{1}/_{3}/33^{1}/_{33}/33^{1}/_{3}$	34.0	8.7	54.5	2.7	8.3
$33^{1}/_{3}/33^{1}/_{3}/33^{1}/_{3}$	34.1	8.0	55.3	2.7	8.4

Resin dispersions were also checked for pH drift and appearance after aging for four weeks at 52°C.

RESULTS

Most hydrolytic stability test results for the two studies are shown using triangular contour maps (*Figures* 3-11). The trends shown in the plots indicate what change in composition is necessary to obtain better hydrolytic stability in waterborne polyester resins. All the plots should be considered together since the trends are indirect indicators of the degree of hydrolysis. In all cases, better hydrolysis resistance is indicated by a smaller percent change in the properties measured.

Diacid Study Dispersion Stability

No phase separation was apparent in any of the resin dispersions after one year of aging at room temperature. Of the diacids studied, the 1,4-CHDA resin exhibited the smallest percent reduction in pH—2% compared with 9% for IPA and 14% for AD (*Figure* 3 and *Table* 10).

After 13 weeks at 52°C, the 1,4-CHDA-based resin dispersion remained virtually clear with no phase separation. The 50:50 IPA: 1,4-CHDA-containing resin dispersion and the 75% IPA-containing resin dispersion were milky white without phase separation. The remaining dispersions were all phase separated (*Table* 11).

Again, the 1,4-CHDA-containing resin showed the least percent reduction in pH—14% compared with 22% for IPA and 26% for AD (*Figure* 4 and *Table* 11).

The improved hydrolytic stability results for 1,4-CHDA, as shown by the least percent reduction in pH, are mirrored in the molecular weight data. The 1,4-CHDA-based resin had the least percent decrease in molecular weight—33% compared with 42% for IPA and 57% for AD after 13 weeks at 52°C (*Figure* 5 and *Table* 11).

The molecular weight data after one year at room temperature did not give statistically significant trends and is, therefore, not shown.

Data for percent reduction in pH and molecular weight after four weeks at 52°C has been included as this is a standard test for hydrolytic stability used in the resins industry (*Figures* 6 and 7).

After seven weeks aging at 52°C, all of the resin dispersions that did not contain 1,4-CHDA phase separated while the resin dispersions containing 1,4-CHDA were only hazed. DMEA was added to the hazed dispersions until they became clear. The amount of DMEA added (as a percentage of the resin dispersion weight) is shown in *Table* 12. Dispersions with higher levels of 1,4-CHDA required the addition of less DMEA illustrating the reduced degree of hydrolysis in these systems.

Changes in physical properties for the enamels from the dispersions aged seven weeks at 52°C were determined by 60° gloss, pencil hardness, forward and reverse impact, crosshatch adhesion, and conical mandrel flexibility (*Table* 13). The primary changes in physical properties were hardness and brittleness which correlate to a decrease in molecular weight of the resins as a result of hydrolysis in dispersion.

The least change in physical properties was seen in the resins containing higher amounts of 1,4-CHDA. IPA contributed less than did AD.

Table 9—Enamel Formulation

Ingredient	Wt %
Resin dispersion (Table 7)[a]	60.7
Cymel 303 melamine resin[b]	9.3
Ti-Pure R-900 TiO_2 pigment[c]	17.8
Fluorad FC-430 flow control agent[d]	0.5
Water (distilled)	11.7
	100.0

Pigment: Binder	37:63
Resin: Crosslinker	70:30

(a) Wt % does not include DMEA content.
(b) Cytec.
(c) DuPont.
(d) 3M.

Table 10—Dispersion pH (Initial vs Final) After One Year at Room Temperature

Acid Composition CHDA/IPA/AD	pH Initial	pH Final
0/50/50	9.0	7.7
50/50/50	8.9	8.2
50/0/50	8.9	7.9
33$^{1}/_{3}$/33$^{1}/_{3}$/33$^{1}/_{3}$	9.0	8.2
100/0/0	8.9	8.7
0/0/100	8.8	7.6
12$^{1}/_{2}$/75/12$^{1}/_{2}$	8.9	8.1

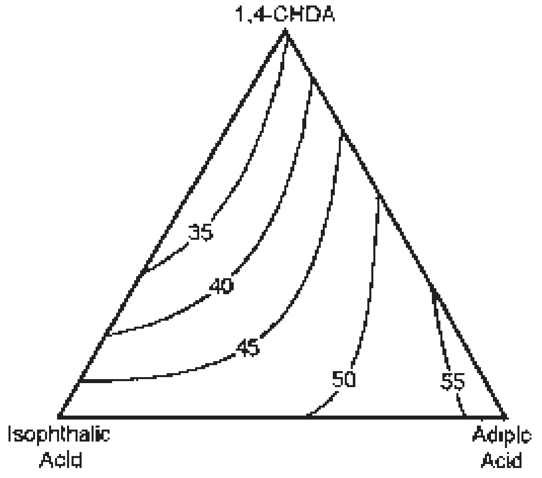

Figure 5—Percent reduction in M_w after 13 weeks at 52°C.

Table 11—Dispersion pH, M_w and Appearance (Initial vs Final) After Four Weeks and 13 Weeks at 52°C

Acid Composition CHDA/IPA/AD	pH Initial	pH Four Weeks	pH 13 Weeks	M_w Initial	M_w Four Weeks	M_w 13 Weeks	Appearance[a] 13 Weeks
0/50/50	9.1	7.5	6.5	10734	7650	5402	Separated
50/50/0	8.9	7.8	7.1	8346	6740	5644	Hazy
50/0/50	8.9	7.7	7.3	10196	7890	5222	Separated
33$^{1}/_{3}$/33$^{1}/_{3}$/33$^{1}/_{3}$	9.0	7.7	6.9	8789	6844	5144	Hazy
100/0/0	9.0	8.5	7.7	12188	10285	8141	Clear
0/0/100	8.7	7.1	6.4	7096	5270	3070	Separated
12$^{1}/_{2}$/75/12$^{1}/_{2}$	8.9	7.6	6.9	12720	8760	7392	Hazy

(a) All dispersions were initially clear.

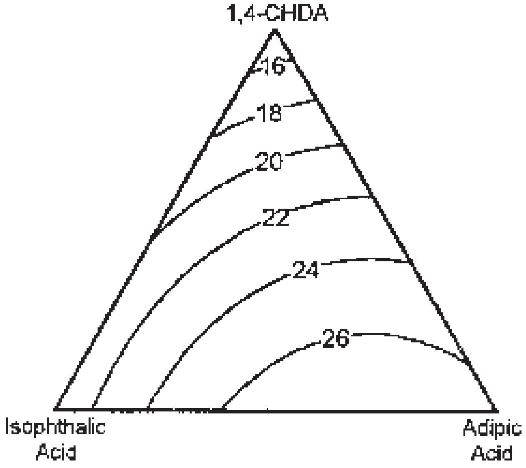

Figure 4—Percent reduction in pH after 13 weeks at 52°C.

Table 12—Percent DMEA Added to Dispersions

Resin CHDA/IPA/AD	Amine Added to Aged Dispersion (Wt %)
50/50/0	1.16
50/0/50	1.08
33$^{1}/_{3}$/33$^{1}/_{3}$/33$^{1}/_{3}$	1.32
100/0/0	0.68

Table 13—Comparison of Physical Properties Between Aged and Unaged Dispersion Enamels

Acid Composition	60° Gloss		Pencil Hardness				Impact Strength (in.-lb)				Cross-hatch Adhesion		Conial Mandrel (% elongation)	
			Unaged		Aged		Unaged		Aged					
CHDA/IPA/AD	Unaged	Aged	Cut	Mar	Cut	Mar	Fwd	Rev	Fwd	Rev	Unaged	Aged	Unaged	Aged
50/50/0	87	75	4H	H	4H	H	20	< 10	20	< 10	3B	3B	2.5	3.0
50/50/0	80	74	4H	H	4H	F	40	< 10	20	< 10	4B	4B	3.9	3.1
50/50/0	81	74	4H	H	4H	F	40	< 10	20	< 10	3B	4B	3.2	3.3
50/0/50	86	65	3H	F	4H	F	100	< 10	80	< 10	4B	4B	20.7	9.7
50/0/50	87	66	4H	F	4H	F	80	10	60	< 10	3B	3B	15.3	9.7
50/0/50	81	65	3H	F	4H	F	120	20	60	< 10	3B	4B	15.1	10.9
$33^{1}/_{3}/33^{1}/_{3}/33^{1}/_{3}$	92	77	3H	F	4H	H	40	< 10	20	< 10	3B	4B	9.6	5.8
$33^{1}/_{3}/33^{1}/_{3}/33^{1}/_{3}$	88	79	4H	F	4H	H	40	< 10	20	< 10	3B	3B	9.7	5.9
$33^{1}/_{3}/33^{1}/_{3}/33^{1}/_{3}$	88	78	3H	F	4H	H	60	< 10	20	< 10	3B	4B	8.6	4.8
100/0/0	92	90	3H	F	3H	F	20	< 10	20	< 10	3B	3B	6.1	4.7
100/0/0	87	83	4H	F	4H	F	40	< 10	20	< 10	3B	3B	6.0	4.3
100/0/0	90	82	4H	F	4H	F	40	< 10	40	< 10	3B	3B	5.4	5.8

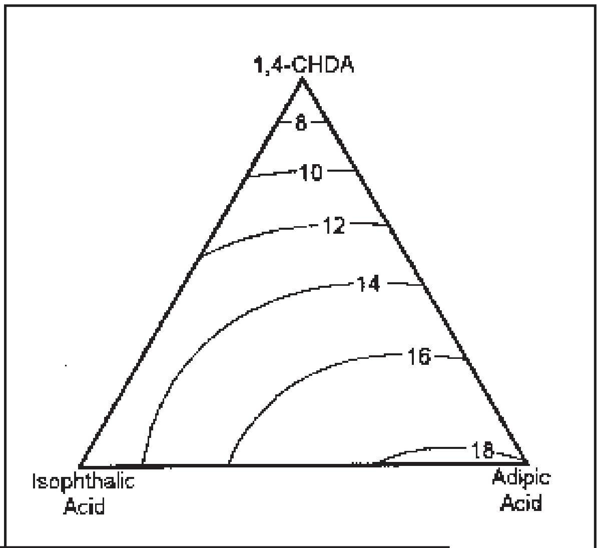

Figure 6—Percent reduction in pH after four weeks at 52°C.

Glycol Study Dispersion Stability

No visual change was apparent in any of the resin dispersions after one year of aging at room temperature. Of the glycols studied, BEPD-based resins exhibited the smallest pH drift—12% (*Figure* 8 and *Table* 14). HPHP showed a moderate improvement in pH drift over NPG glycol—15% compared to 19%.

For forward impact resistance, BEPD produced resins that showed no change after aging for one year at room temperature, the NPG-based system lost 84% and the HPHP-based system lost 40% in comparison with the unaged systems (*Figure* 9 and *Table* 14).

The change in MEK double-rub resistance for the BEPD-based system was much lower than for any other system studied (*Figure* 10 and *Table* 14).

After four weeks at 52°C, no phase separation was apparent in any of the resin dispersions. The BEPD-containing resin showed the least percent reduction in pH—15% compared with 21% for HPHP and 24% for NPG glycol (*Figure* 11 and *Table* 15).

All results indicated that resins based on BEPD are much more resistant to hydrolysis than those based on HPHP and NPG glycol.

DISCUSSION

The electron donating or withdrawing characteristics of a carboxylic acid substituent influence the dissociation constant of the acid. Electron-withdrawing groups raise the dissociation constant and increase the partial positive charge on the carbonyl carbon. A larger partial positive charge makes the carbon more susceptible to nucleophilic attack.[2] Therefore, diacids such as IPA with high dissociation constants[6] should form ester bonds which are less stable against base catalyzed hydrolysis.

However, polar interactions are not important in acid catalyzed hydrolysis.[2] Although electron-donating sub-

Table 14—Dispersion pH and Cured Enamel Properties (Initial vs Final) After One Year at Room Temperature

Glycol Composition	pH		Forward Impact (in.-lb)		MEK Double-Rubs	
BEDP/HPHP/NPG	Initial	Final	Initial	Final	Initial	Final
100/0/0	8.8	7.7	152	152	64	72
50/50/0	8.4	7.4	168	160	40	86
0/100/0	8.6	7.3	272	158	62	82
0/0/100	8.8	7.1	152	24	76	268
50/0/50	8.9	7.6	200	36	71	134
0/50/50	8.5	7.2	232	67	52	194
$33^{1}/_{3}/33^{1}/_{3}/33^{1}/_{3}$	8.3	7.3	264	71	50	134
$33^{1}/_{3}/33^{1}/_{3}/33^{1}/_{3}$	8.4	7.3	264	70	58	121

stituents should allow the protonation step to proceed more quickly, they also inhibit the nucleophilic attack by water. Electron withdrawing groups would simply inhibit the protonation. Since acid-catalyzed hydrolysis requires both an electrophilic and nucleophilic attack of the carbonyl, polar effects are inconsequential.

Resonance of a carbonyl group with an α,β-unsaturated substituent such as the aromatic ring in IPA stabilizes the carbonyl against attack.[2] For example, esters of benzoic acid show marked resistance to hydrolysis despite the fact that the phenyl group provides little steric hindrance.[2]

Atoms in the fifth, sixth, and seventh positions from the carbonyl oxygen interfere with esterification and hydrolysis by physically obstructing the carbonyl carbon.[3,4] Since polar effects are unimportant in acid-catalyzed esterification, a comparison of acid-catalyzed esterification rates shows relative steric shielding for saturated diacids. Slow esterification rates associated with aromatic diacids are caused by resonance; therefore, a direct comparison with aliphatic diacids is not possible. It is known that the steric hindrance for a phenyl ring is extremely low unless ortho substitution is present.[2]

IPA has dissociation constants that are an order of magnitude higher than those for AD and 1,4-CHDA and should, therefore, produce esters with less hydrolytic stability in alkaline conditions (*Table* 16). However, resonance of its carbonyls with the aromatic ring should stabilize IPA against esterification and/or hydrolysis under acidic conditions.

Comparing esterification rates for the saturated diacids shows that cis 1,4-CHDA is the most sterically shielded diacid followed by trans 1,4-CHDA and finally AD. Although IPA has the slowest esterification rate due to resonance, it has no ortho substitution to provide steric shielding and, therefore, should have the lowest steric shielding of the three diacids.

To further understand the results of the polyester studies, we can draw upon information from a separate study of model diesters. To determine the hydrolysis rates of the simple bis-NPG esters of AD, IPA, and 1,4-CHDA, hydroxy functional diesters were solubilized in a mixture of dioxane and water and aqueous solutions buffered to acidic (pH 4.5) and basic (pH 8.9) conditions.[7]

Table 15—Dispersion pH (Initival vs Final) After Four Weeks at 52°C

Glycol Composition BEPD/HPHP/NPG	Initial	Final
100/0/0	8.8	7.5
50/50/0	8.4	7.0
0/100/0	8.6	6.8
0/0/100	8.8	6.7
50/0/50	8.9	7.2
0/50/50	8.5	6.8
$33^{1}/_{3}/33^{1}/_{3}/33^{1}/_{3}$	8.3	6.9
$33^{1}/_{3}/33^{1}/_{3}/33^{1}/_{3}$	8.4	6.9

The results of the model study given in *Figure* 12 shows that although the hydrolysis rate of IPA is very low in acidic conditions, the basic conditions normally encountered in waterborne polyester coating formulations make IPA esters highly susceptible to hydrolysis. The aliphatic diacids 1,4-CHDA and AD were much more stable than IPA under alkaline pH conditions, and the higher steric shielding of 1,4-CHDA gives it an advantage over AD. This follows the established theory of ester hydrolysis as defined by the polar, resonance, and steric effects, but it contradicts conventional polyester wisdom regarding the relative stability of IPA-based resins versus AD-based resins (the “hard to make—hard to break” assumption).

In the polyester resin study of diacids, the order of hydrolytic stability was not the same as seen in the model study. In the polyester study, 1,4-CHDA continued to produce the most stable esters; however, IPA showed more hydrolytic stability than AD as expected from common experience.

A possible explanation can be found by comparing the solubility of each diacid in water at 100°C (*Table* 16). AD has a solubility several orders of magnitude greater than the other diacids. Thus, a polyester containing IPA or 1,4-CHDA is much more hydrophobic than one containing AD. By making the polyester chains more hydrophobic, water molecules will

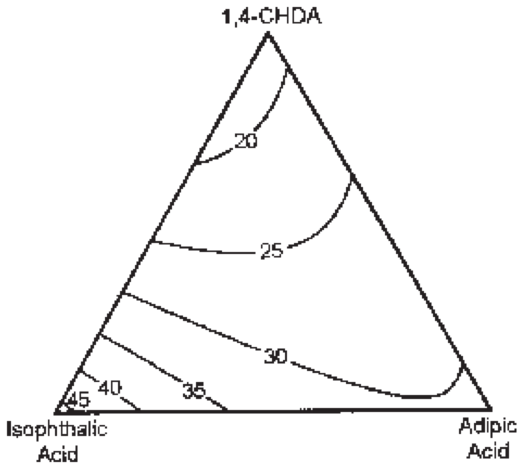

Figure 7—Percent reduction in M_w after four weeks at 52°C.

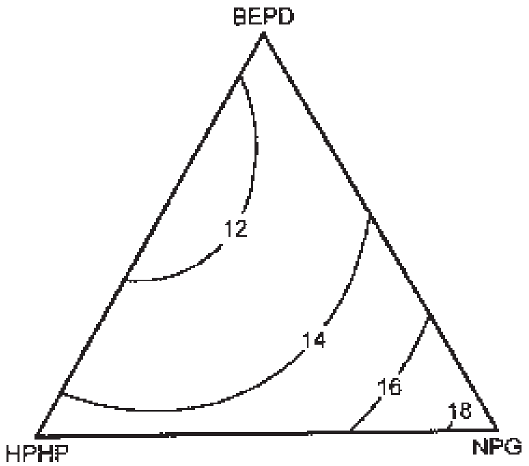

Figure 8—Percent reduction in pH after one year at room temperature.

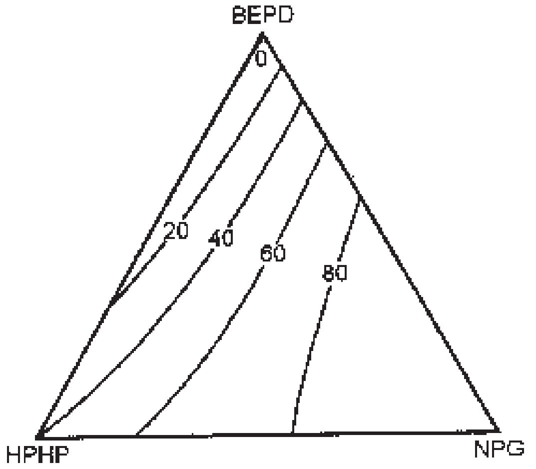

Figure 9—Percent reduction in forward impact resistance after one year at room temperature.

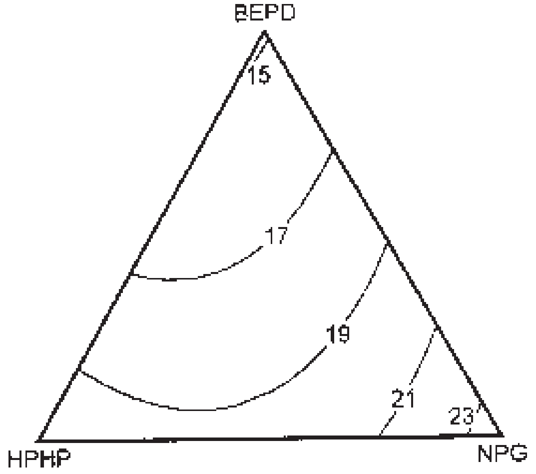

Figure 11—Percent reduction in pH after four weeks at 52°C.

Table 16—Diacid Properties

	Dissociation Constants (K x 10^{-5})		Esterification Rates[a] (K x 10^{-3}, $(kg/mol)^2\ min^{-1}$, @ 210°C)		Water Solubility (g/100g water, @ 100°C)
Diacid	**K_1**	**K_2**	**K_1**	**K_2**	
cis 1,4-CHDA	—	—	2.7	2.8	—
trans 1,4-CHDA	6.6	0.38	4.4	4.6	1.3
Adipic Acid	3.7	0.39	5.6	6.1	290
Isophthalic Acid	24	2.5	2.2	2.9	0.24

(a) Rates with a large excess of NPG glycol and all acids dissolved.

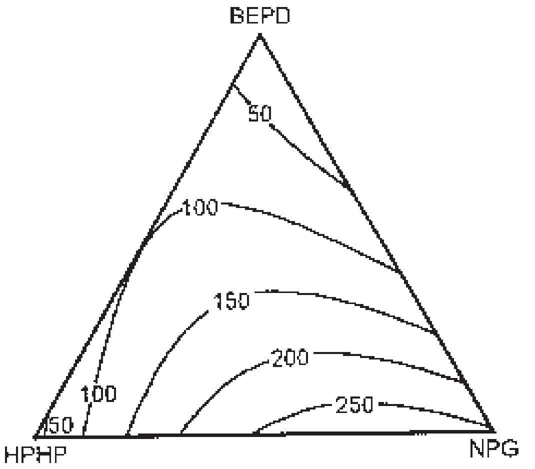

Figure 10—Percent increase in MEK double-rub resistance after one year at room temperature.

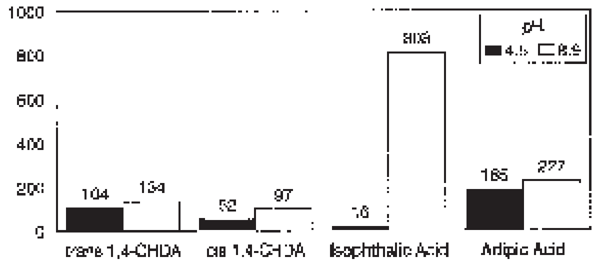

Figure 12—Hydrolysis rates of diesters at 120°C ($10^6\ min^{-1}$).

Table 17—Glycol Properties

Glycol	Molecular Weight (g/mol)	Solubility in Water[a] (Wt % Glycol)	Steric Shielding Atoms Provided to Ester Links 5th	6th	7th
NPG	104	64	3	3	9
BEPD	160	0.8	3	3	9
HPHP	204	13	3	3	8 or 9

(a) Room temperature.

tend to interact less with the esters. Also, the water will tend to force the polymer to coil upon itself and/or to interact more closely with other organic molecules such as cosolvent or other polymer molecules.

The results of the glycol study also support this hypothesis that hydrophobicity is an important factor in the hydrolysis of waterborne polyester resins. *Table* 17 contains the solubility of each glycol in water at room temperature. BEPD is the least water-soluble glycol in the study, while NPG glycol is the most soluble. A resin containing BEPD would be much more hydrophobic than one containing HPHP which, in turn, would be more hydrophobic than one containing NPG. As no other differences in steric shielding, polarity, or resonance are evident (*Table* 17), the hydrophobic effect should be the dominant factor governing differences in hydrolysis of the polyester resins in the glycol study.

CONCLUSIONS

Ester hydrolysis theory as derived from simple ester studies does not fully predict the hydrolytic stability of polyester resins. Established hydrolysis theory and model studies predict that AD would produce more stable polyesters than IPA due to polar effects. However, it is well-known by resin formulators and confirmed here that IPA-based polyesters demonstrate greater hydrolytic stability in comparison to AD. This switch in relative stability may be attributed to the high hydrophobicity of IPA compared to AD.

Established hydrolysis theory does, however, accurately predict order of stability for polyesters when the monomers being compared have similar hydrophobicity. When 1,4-CHDA and IPA are compared, the theory accurately predicts that polar effects reduce the stability of IPA esters relative to 1,4-CHDA esters under base catalyzed conditions. Therefore, the established hydrolysis theory holds for polyesters when the hydrophobic effect is kept relatively constant.

The hydrophobic effect may be more clearly observed in the glycol study. As all the factors described by established hydrolysis theory are similar for the three glycols, no differences in hydrolytic stability would have been predicted. However, the hydrolytic stability of polyesters made from the glycols was directly proportional to the increasing hydrophobicity of the glycol component. Apparently, hydrophobic effects govern polyester hydrolysis when all established hydrolysis theory factors are held constant.

In practical terms, diacids should be chosen based on the dissociation constants and water solubility as well as steric shielding when optimizing for hydrolytic stability. The cycloaliphatic structure of 1,4-CHDA makes it possible to have low dissociation constants and low water solubility in the same molecule. This combination of properties is not present with either IPA or AD.

When optimizing for hydrolytic stability with the glycol portion of a polyester, glycols should be chosen based on water solubility as well as steric shielding. At a solubility in water of 0.8 weight percent, BEPD is ideally suited for improving the hydrolytic stability of waterborne polyester resins in comparison to other commercially available glycols.

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