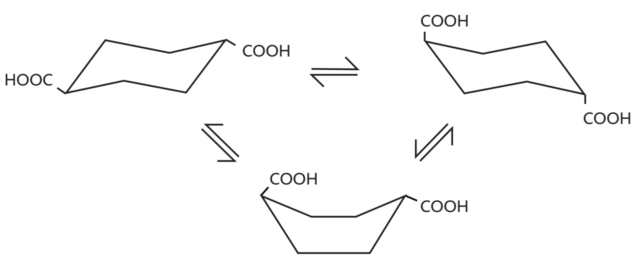
Improved coil coating performance with Eastman™ 1,4-CHDA

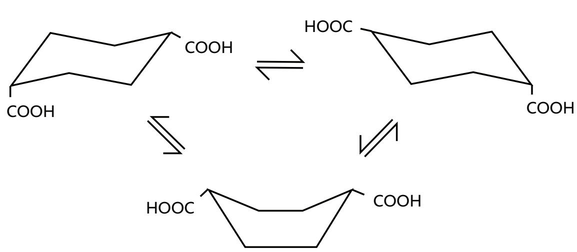
Cycloaliphatic structure of Eastman™ 1,4-CHDA (1,4-cyclohexanedicarboxylic acid)

Movement between the boat and chair conformations equals coating flexibility.

Trans-isomer conformations



Cis-isomer conformations



Introduction

The chemical structure of Eastman™ 1,4-CHDA (1,4-cyclohexanedicarboxylic acid) offers the resin and polymer industry a unique diacid intermediate. The heart of the molecule is a 1,4-substituted cyclohexane ring. The cycloaliphatic structure (illustrated on left) is responsible for many of the desirable performance properties that 1,4-CHDA imparts to polyester resins and enamels. Compared with aromatic and aliphatic diacids, some of the benefits of using 1,4-CHDA are that it offers an incremental improvement in hardness/flexibility ratio over a traditional 1:1 blend of hard aromatic and flexibilizing aliphatic diacids. The stain/detergent/salt spray resistance benefits are especially useful in appliance-grade coil coatings (Eastman publication N-330). Resins containing 1,4-CHDA are also used in stabilized exterior coil coatings.

The performance benefits of Eastman™ 1,4-CHDA in coil coatings are described herein.

Hardness and flexibility

The cycloaliphatic structure of Eastman™ 1,4-CHDA with 1,4-ring substitution results in a superior combination of hardness and flexibility without major performance weaknesses.

Stain/detergent/salt spray resistance

Eastman™ 1,4-CHDA imparts better stain/detergent/salt spray resistance than linear aliphatic diacids, such as AD (adipic acid), because 1,4-CHDA offers more steric shielding of the ester linkages.

Processability

Eastman™ 1,4-CHDA reacts faster than aromatic diacids because of its greater solubility in molten glycols.

Experimental details

A statistically designed mixture experiment was used to compare Eastman™ 1,4-CHDA with Eastman™ purified isophthalic acid (PIA) and AD. Table 1 shows the general composition and the obtained property range of the eight resins used in this study. The combination of Eastman NPG™ glycol and 1,6-hexanediol (1,6-HD) was a constant for all the resins.

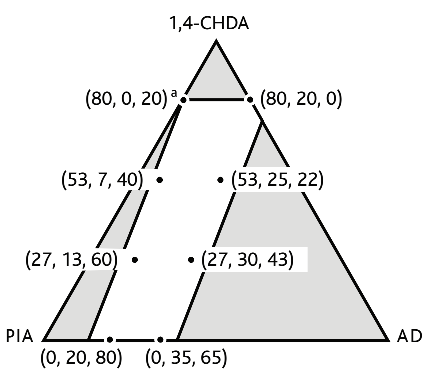
The diacid ratio for each of the eight resins selected is shown in the experimental design, Figure 1. Each point represents a unique resin composition.

Table 1 Resin composition and properties

Resin composition	
Eastman NPG™ glycol/1,6-HD/diacid intermediates Molar ratios—0.89/0.16/1.00	
Resin properties	
Final acid number, mg KOH/g resin	2–4
Molecular weight (M_n)[a]	4200–4600
Hydroxyl number, mg KOH/g resin	21–29
Weight percent solids in xylene	69–73

[a]*A refractive index detector was used in the GPC molecular weight determination.*

Figure 1
Experimental design



[a]*Eastman™ 1,4-CHDA, AD, and Eastman™ PIA ratio in all compositions listed here.*

The resins described in Figure 1 and Table 1 were used to make enamels based on the formulation in Table 2. All the enamels were adjusted to the same calculated weight percent solids with the solvent blend. The enamels were drawn down onto Bonderite™ 721 pretreated 24-gauge aluminum 3003 H14 test panels and cured for 30 seconds at 313°C (595°F) to obtain a peak metal temperature of 232°C (450°F). Cured enamels ranged in thickness from 0.69 to 0.77 mil and exhibited MEK resistance to breakthrough of 120 to 210 double rubs. An automated drawdown device was used to maintain film consistency.

Table 2 Enamel formulation

Ingredients	Wt%
Polyester resins (at 71 wt% solids)	40.0
Cymel™ 301 melamine resin[a]	3.2
Ti-Pure™ R-960 TiO_2 pigment[b]	31.8
Acrylic flow control additive	0.5
Blocked dinonylnaphthalene sulfonic acid	2.1
Solvent blend (Solvesso[c] 150:ethylene glycol diacetate, 1:1)	22.4
	100.0
Pigment:binder ratio	1:1
Polyester:melamine ratio	9:1

[a]*Cytec*
[b]*DuPont*
[c]*Exxon*

Results

Results obtained through the determination of 50–60 various resin and enamel criteria are found in the following contour maps. Regression analysis was used to interpret the data. The contour plots in the following triangles all have statistical correlation with the data generated. Only the area defined by the experimental design is shown. Extrapolating these results into other regions of the triangle is invalid. As with our previous "triangle study" (Eastman publication N-335), the **trends shown in the plots, rather than the absolute values, are the significant information.**

At the top of each page is a triangular symbol illustrating the effect of each diacid intermediate on the performance property. An explanation for these symbols follows:

▲ Desired performance increases with diacid content.

◭ No significant effect on performance when diacid content is varied.

△ Desired performance decreases with increasing diacid content.

Resin color and viscosity

▲ **Eastman™ 1,4-CHDA**

▲ **AD**

△ **Eastman™ PIA**

Resin solubility

△ **Eastman™ 1,4-CHDA**

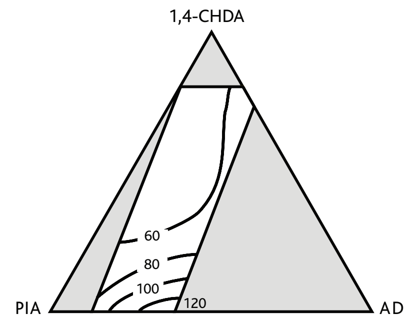
▲ **AD**

△ **Eastman™ PIA**

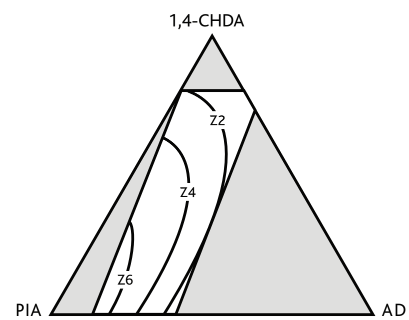
Care must be taken with the amount of Eastman™ 1,4-CHDA or Eastman™ PIA in a simple (four-component or less) resin system. The "sweet spot" or desired area, in terms of resin solubility, appears to be near the center of the triangle. Resins made with 2 diacids and dissolved in the solvent blend averaged only 15 days to a medium degree of haze, while 3-diacid component resins averaged 155 days to a similar haze point.

1,4-CHDA appears to offer a definite advantage in the color of the final resin and acts as a hybrid of aromatic and aliphatic diacids when viscosity is the performance criteria. An interesting point is the similarity in the viscosity trends of these triangles and those in our previous work (Eastman publication N-335), even though the resins are different.

Color APHA

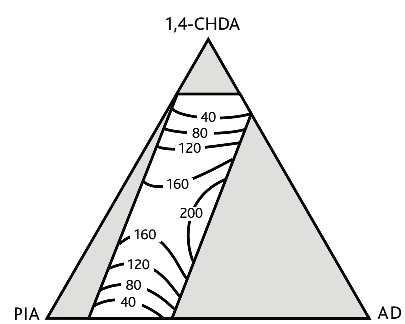


Viscosity



Gardner at 70% solids, 25 °C

Haze



70% solids, days to medium haze

Hardness

Eastman™ 1,4-CHDA

AD

Eastman™ PIA

Flexibility

Eastman™ 1,4-CHDA

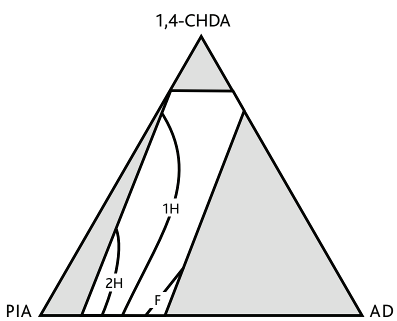
AD

Eastman™ PIA

Eastman™ PIA excels in hardness but offers little or no flexibility, while AD performs in the opposite manner. Both of these diacids are strong in one performance area but weak in the other.

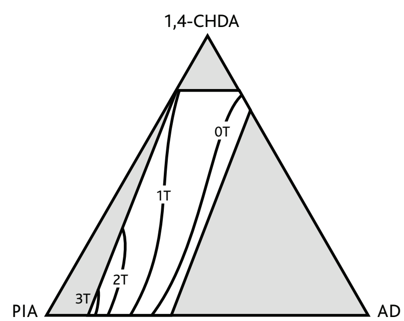
Eastman™ 1,4-CHDA exhibits the superior combination of hardness and flexibility required for coil coatings without the shortcomings of PIA or AD. This combination of hardness and flexibility should make 1,4-CHDA the "diacid of choice" for high-performance coil coating applications.

Hardness



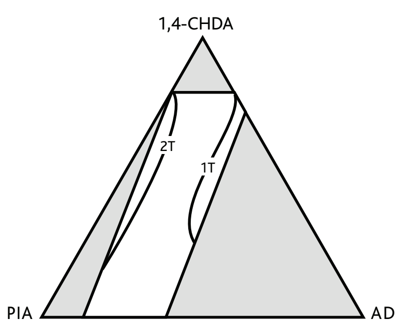
Pencil, passed to breakthrough

T-Bends[a]



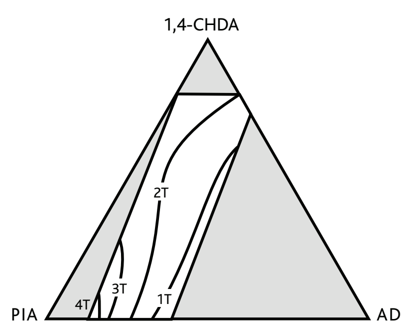
Original

T-Bends[a]



After 30 seconds at 500°F

T-Bends[a]



After 5 minutes in boiling water

[a]*T-bends were checked with tape and showed no crack under unmagnified visual inspection.*

Stain Resistance

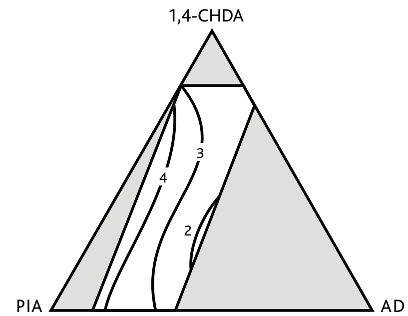
◭ **Eastman™ 1,4-CHDA**

△ **AD**

▲ **Eastman™ PIA**

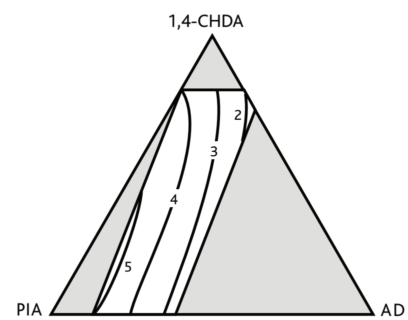
The difference in contribution to stain resistance between Eastman™ 1,4-CHDA and PIA seems to be small, while AD has a definite negative effect on this measure of performance.

Stain resistance[a]



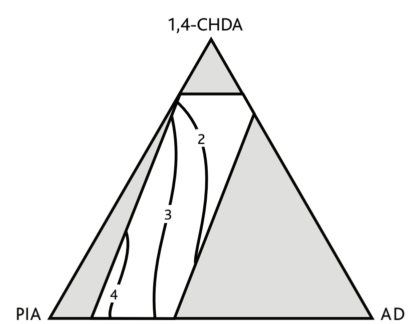
Mustard, 24 h
covered and uncovered

Stain resistance[a]



Grape juice, 24 h covered

Stain resistance[a]



Lipstick, 24 h covered and uncovered

[a]*Stain resistance panels were washed with Dawn™ detergent, rinsed with water, and wiped dry before evaluation.*

Scale: 5 = no effect; 4 = slight effect; 3 = moderate effect; 2 = considerable effect; 1 = severe effect.

Detergent/salt spray resistance

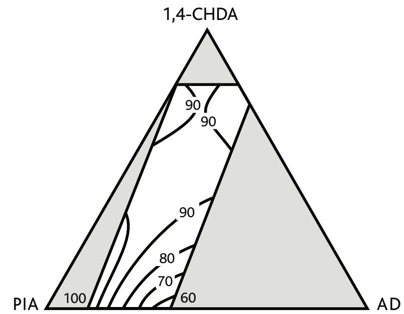
Eastman™ 1,4-CHDA

AD

Eastman™ PIA

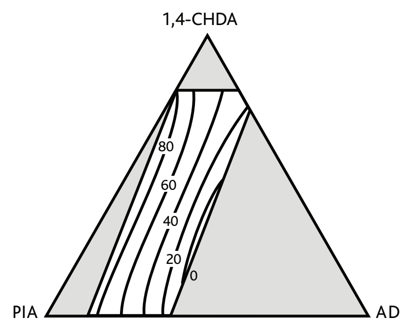
AD appears to be the controlling factor on detergent resistance with Eastman™ 1,4-CHDA and Eastman™ PIA performing similarly. High levels of 1,4-CHDA offer a very flat, good performing area for salt spray resistance. A much greater fluctuation in performance is observed with high PIA content and increasing amounts of AD. Sufficient correlation to generate Cleveland™ humidity contour plots was not obtained.

Salt spray resistance[a]



1,000 h, 20° gloss retention, %

Detergent resistance[b]



5 days, 20° gloss retention, %

[a]*ASTM method B117-64 was used.*

[b]*A 2%–3% (by weight) solution of Tide™ detergent (pH 10–11) was used in ASTM method 02248-73.*

Summary

	Eastman™ 1,4-CHDA	AD	Eastman™ PIA
Resin color and viscosity	▲	▲	△
Resin solubility	◭	▲	△
Hardness	◭	△	▲
Flexibility	◭	▲	△
Stain resistance	◭	△	▲
Detergent/salt spray resistance	◭	△	▲

This statistically designed study has demonstrated the performance advantages of Eastman™ 1,4-CHDA in coil coatings. As indicated by the symbols above, Eastman™ purified isophthalic acid (PIA) and AD are strong in some performance criteria but have weaknesses in others. Because 1,4-CHDA has performance strengths (resin processability and a superior combination of hardness and flexibility) with no major disadvantages, it should be considered the "diacid of choice" for high-performance coil coatings. For optimal performance, the coil resin should be based on a blend of 1,4-CHDA and PIA.

The cycloaliphatic structure of 1,4-CHDA is responsible for the unique performance properties that it imparts to coatings. The 1,4-substitution allows for maximum utilization of movement from the cyclohexane ring. This movement is responsible for the flexibility that 1,4-CHDA imparts. The cycloaliphatic structure is also responsible for the hardness and stain/detergent/salt spray resistance of 1,4-CHDA-based coatings.

Coil coating enamels described herein were evaluated for exterior durability both in Florida and in a carbon arc weatherometer. There was no reliable correlation between the two techniques or within the Florida study. As a result, each end user should generate weathering data for any formulation intended for exterior use.

The use of stabilizers as a means of improving the weathering performance of these formulations should be investigated. Studies at Eastman with higher solids/high gloss formulations have revealed that the weatherability of enamels based on Eastman™ 1,4-CHDA is enhanced more with hindered amine light stabilizers (HALS) than with ultraviolet absorbers (UVAs). In addition, combinations of Eastman™ PIA (>50 mole %) with 1,4-CHDA (for flexibility) have maintained excellent levels of gloss retention after prolonged exposure to QUVA-340. The use of QUVB-313 is not suggested as a screening tool because the low wavelength portion of the exposure spectrum can lead to anomalous results.

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