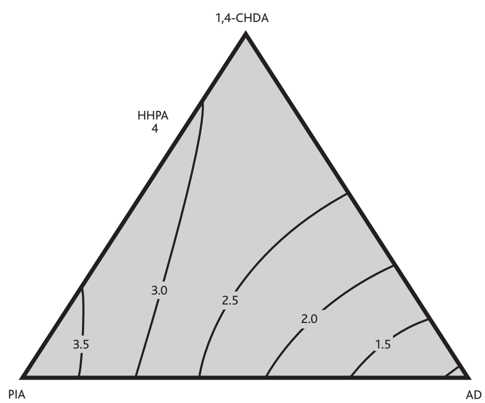
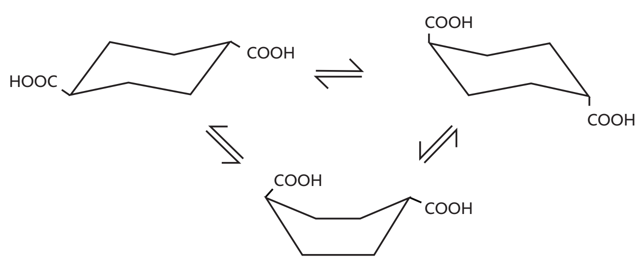
A statistical comparison of Eastman™ 1,4-CHDA, Eastman™ PIA, AD, and HHPA in a high-solids resin system based on Eastman TMPD™ glycol



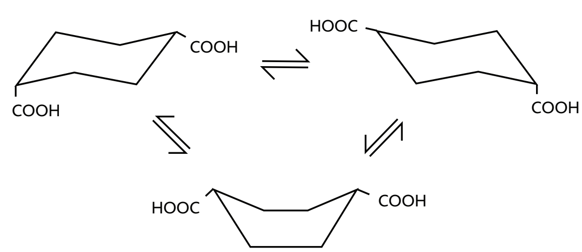
Cycloaliphatic structure of Eastman™ 1,4-CHDA (1,4-cyclohexanedicarboxylic acid)

Movement between the boat and chair conformations equals coating flexibility.

Trans-isomer conformations

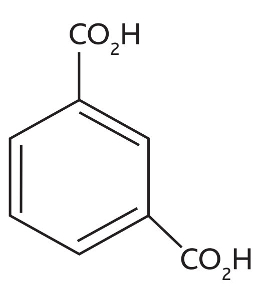


Cis-isomer conformations



Aromatic structure of Eastman™ PIA (Purified isophthalic acid)

Rigid aromatic cyclic structure equals excellent hardness.



Introduction

Eastman™ 1,4-CHDA and Eastman™ PIA are two of the many diacids used in the resin industry with each providing desirable performance properties. Both products are successfully used throughout the resin manufacturing industry and offer the resin chemist latitude in developing resins with desirable property ranges.

Eastman 1,4-CHDA provides resins with a unique balance of flexibility, hardness, and resistance properties. The 1,4-substitution of the acid groups on the cyclohexane ring provides maximum movement of the ring structure and thus provides resins with enhanced flexibility without significantly sacrificing hardness or stain resistance.

Eastman PIA provides resins with excellent hardness, resistance properties, and low color as expected from this widely used aromatic diacid. The aromatic ring of Eastman PIA yields harder resins with less flexibility.

Both products have a basic cyclic ring structure generally associated with providing resins with excellent thermal stability as well as good stain resistance when compared to linear aliphatic diacids. The remainder of this publication will focus on comparisons and subsequent beneficial trends of incorporating Eastman™ 1,4-CHDA and/or Eastman™ PIA in resin systems versus the other commonly used diacids, adipic acid (AD) and hexahydrophthalic anhydride (HHPA). A complete listing of Eastman 1,4-CHDA and Eastman PIA literature is provided at the end of this publication.

Performance benefits

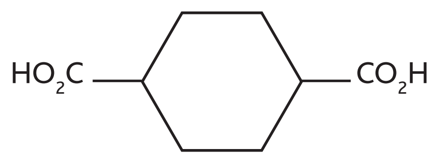
Eastman™ 1,4-CHDA

Coatings performance

- Hardness/flexibility balance
- Hydrolytic stability
- Stain resistance
- Chemical resistance
- Corrosion resistance
- Detergent resistance

Resin processing

- Rapid reactivity
- Low resin color



CAS: 1076-97-7

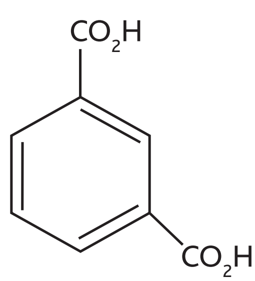
Eastman™ PIA

Coatings performance

- Excellent hardness
- Excellent corrosion and stain resistance
- Excellent hydrolytic stability of coatings and gel coats
- Excellent thermal stability
- Low resin color
- Moderate resin solubility

Resin processing

- Moderate solubility in molten glycols for good processing rates



CAS: 121-91-5

Background of experiment

A statistically designed experiment was chosen to compare Eastman™ 1,4-CHDA with Eastman™ PIA and adipic acid (AD). This study was based on Eastman's current high-solids resin formulation HS-3-6T based on Eastman TMPD™ glycol (see publication N-362). The experimental design is shown in the following triangle with a dot representing each resin included in the study. A dot at the corner of the triangle indicates 100 weight % usage of that diacid in the resin; a dot at the midpoint of a triangle side represents a 1:1 molar blend of those two acids on that triangle side. The dot at the center of the triangle means equal molar amounts (1:1:1) of all three diacids that were used in the resin. While these seven resins were adequate to provide the data for this study, two additional resins containing 75:25 and 25:75 molar blends of 1,4-CHDA with AD were also examined because of their availability. A resin containing HHPA (hexahydrophthalic anhydride) as the total diacid component was included as a reference point for its comparison with the other three diacids. Table 1 shows resin compositions and properties. All resins were cooked to similar acid number and molecular weight (M_n, number average).

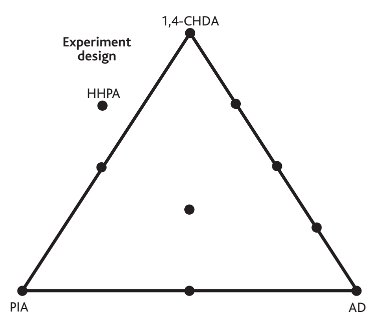


Table 1 **Resin compositions and properties**

Resin compositions	
Eastman TMPD™ glycol/TMP[a]/acid intermediates	
Molar ratio—2.97/0.27/2.00	
Resin properties	
Final acid number, mg KOH/g resin	5–7
Molecular weight (M_n, number average)	900–1,000
Hydroxyl number (calculated), mg KOH/g resin	190–200
Weight percent solids in xylene (calculated)	85
Number of days to haze at room temperature	>180

[a]*Two-stage addition of trimethylolpropane (TMP)*

The resins described were made into enamels using the formulation in Table 2. Additional solvent blend was added to each enamel to obtain #4 Ford cup viscosity of 30 to 31 seconds, except for the 100 weight % AD and the 3:1 AD:Eastman™ 1,4-CHDA enamels, which had an initial viscosity of 25 seconds and were used "as is." The enamels were sprayed onto Bonderite™ 37 pretreated 20-gauge cold-rolled steel test panels and were cured for 20 minutes at 149°C (300°F) with a cured film thickness of 1.5 to 1.8 mils.

Table 2 **Enamel formulation**

Ingredients	Weight %
Polyester resin (85 weight % N.V.)	42.8
Cymel™ 303 melamine resin[a]	12.2
Ti-Pure™ R-900 TiO_2 pigment[b]	32.5
p-Toluenesulfonic acid catalyst (40 weight % N.V.)	0.4
Fluorad™ FC-430 flow control (20 weight % N.V.)[c]	0.5
Solvent blend[d]	11.6
Total	100.0
Pigment:binder ratio	40:60
Polyester:melamine ratio	75:25

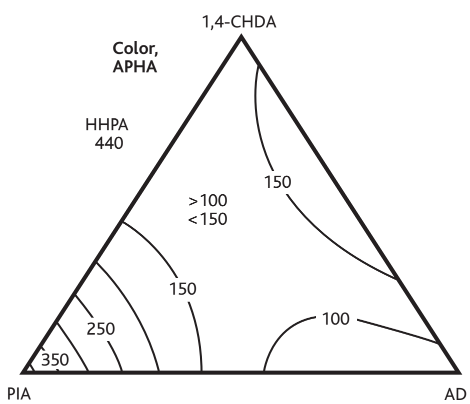
[a]*Cytec*
[b]*DuPont*
[c]*Product is no longer available. 3M suggests FC-4430 as a replacement.*
[d]*Eastman™ MAK:Eastman™ EEP:*n*-butanol in the weight ratio 4:1:1*

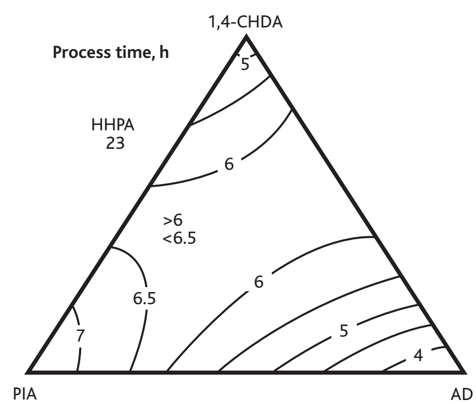
Experiment results

The results obtained through the determination of various resin and enamel properties are found in the following triangular contour maps. The lone HHPA result for each determination is located near the upper left portion of the triangle. Regression analysis was used to interpret the data. **The trends shown in these plots, rather than the absolute values, are the significant information.** Knowledge of trend direction (or change in resin composition) is necessary to obtain the best combination of desired properties in a resin or enamel.

Resin processability

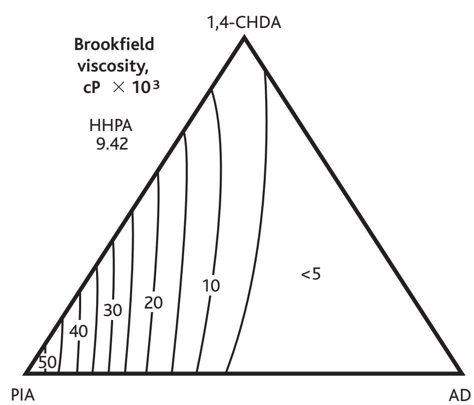
Resin processability was measured by final resin color and processing times. Generally, longer processing times and higher temperatures correlate with increasing resin color. This trend is well illustrated in the following triangles. Solubility in heated glycol is an important attribute when considering resin processing. Those diacids with greater glycol solubility, such as AD, process faster and result in lower resin color. Eastman™ PIA processes slower than Eastman™ 1,4-CHDA or AD due to this lower glycol solubility. Processing time and resin color can be improved by partial replacement of Eastman PIA with Eastman 1,4-CHDA or AD. HHPA was the most difficult material to process in this study as seen in the comparative data and thus resulted in the highest color resin.

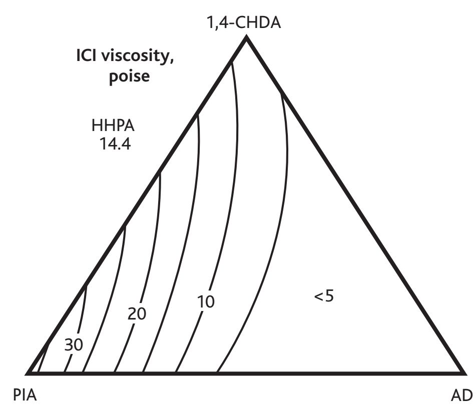


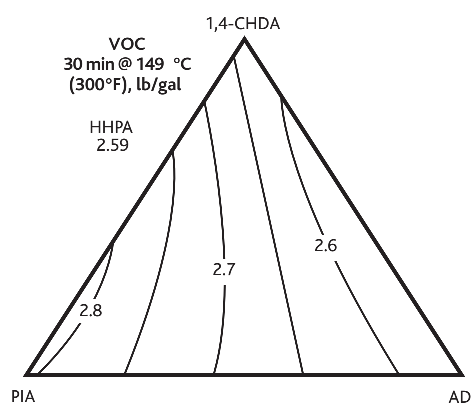


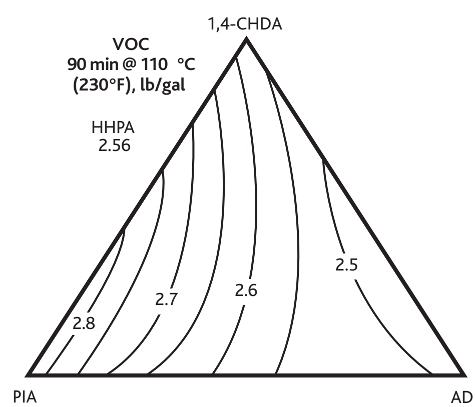
Resin viscosity and enamel VOC

The ICI viscosity at 38°C (100°F) for the neat resins and the Brookfield viscosity for the resins in solution (85 weight % in xylene) illustrate how AD, Eastman™ 1,4-CHDA, and Eastman™ PIA structure influences resin viscosity. Both neat resin viscosity and solution viscosity decrease as AD level increases. Eastman 1,4-CHDA behaves similarly to AD. Viscosity is an important parameter for formulating solventborne enamels. Low viscosity resins generally dissolve at higher solids levels than do high viscosity resins. This translates to less solvent needed to achieve acceptable application viscosities. Therefore, lower viscosity resins tend to provide lower VOC. The following triangles illustrate the effect resin viscosity has on enamel VOC. HHPA provided resins with viscosity and VOC values similar to those of Eastman 1,4-CHDA.





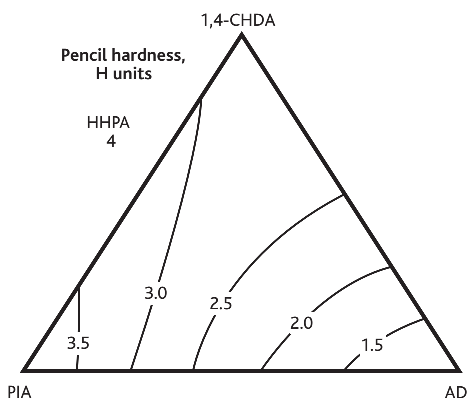


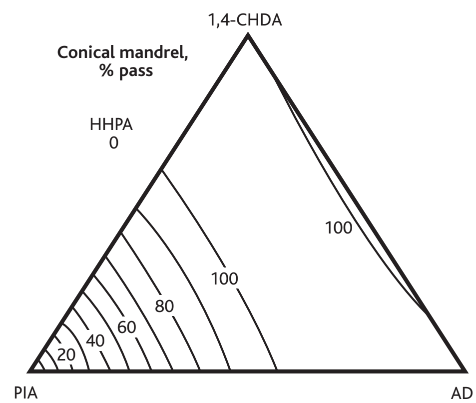


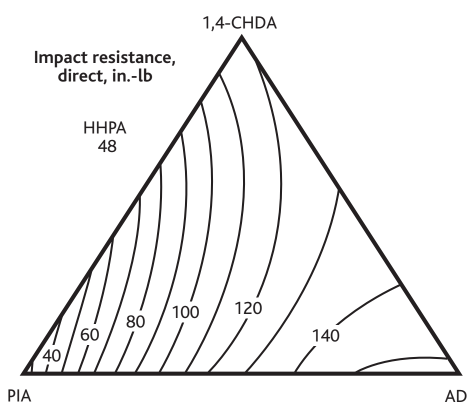
Hardness and flexibility

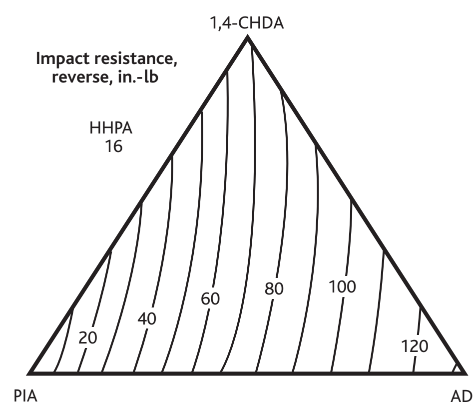
Hardness was measured by pencil hardness to mar (scratch). Eastman™ PIA provided resins with maximum hardness while AD-based resins were softest. Resins based on Eastman™ 1,4-CHDA provided a compromise and trended to be more like Eastman PIA than AD. Resins based on HHPA were similar in hardness to those based on Eastman PIA.

Flexibility was measured by 1⁄8-inch conical mandrel, direct impact resistance, and the more severe reverse impact resistance. The resin hardness imparted by Eastman PIA and HHPA results in poor flexibility as shown in the following triangles. The conical mandrel test shows Eastman 1,4-CHDA to be as flexible as AD. However, this is not the case when comparisons are made using more sensitive impact resistance testing, which shows the trend that AD resins are more flexible than those resins based on the other three diacids. Incorporation of Eastman 1,4-CHDA or AD in combination with Eastman PIA results in improved flexibility. However, Eastman 1,4-CHDA does not adversely affect hardness as clearly seen from the hardness triangle. Flexibility of resins prepared from HHPA was similar to Eastman PIA-based resins.



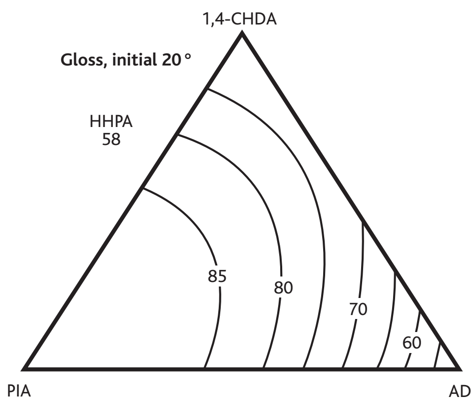


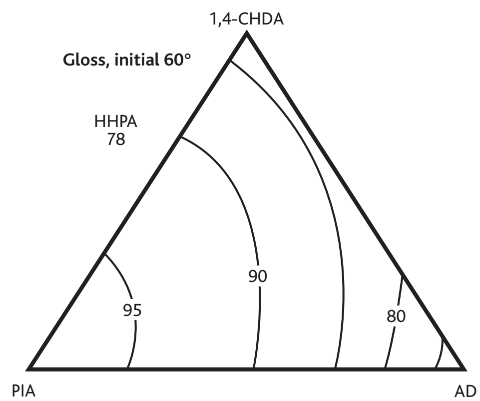




Initial gloss

Initial 20° and 60° glosses of the enamels were determined with Eastman™ PIA-based resins exhibiting the highest initial values. Addition of Eastman™ 1,4-CHDA resulted in a drop in gloss. However, high levels of AD were more detrimental than high levels of Eastman 1,4-CHDA. The initial gloss values for HHPA were similar to those obtained with AD.

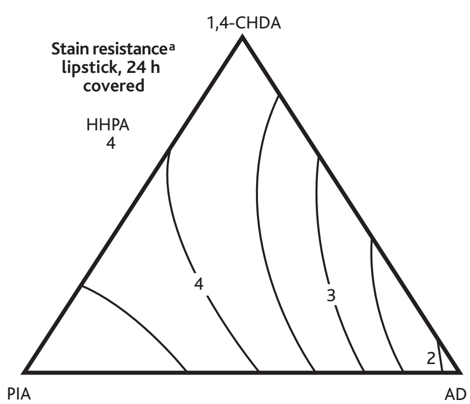


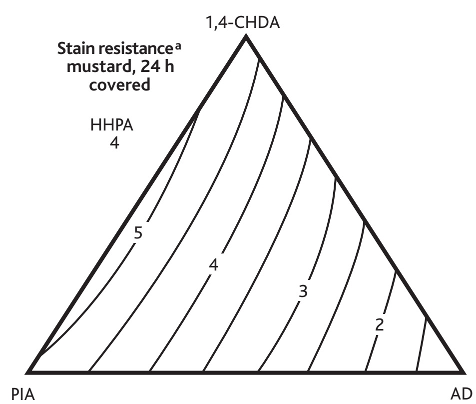


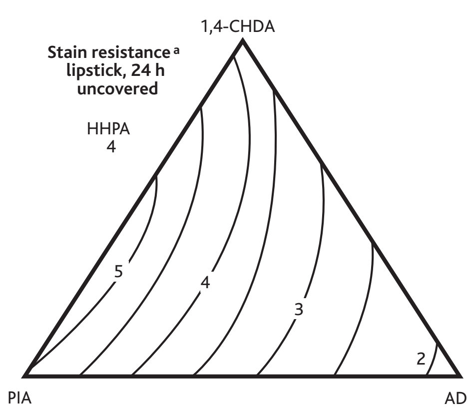
Stain resistance

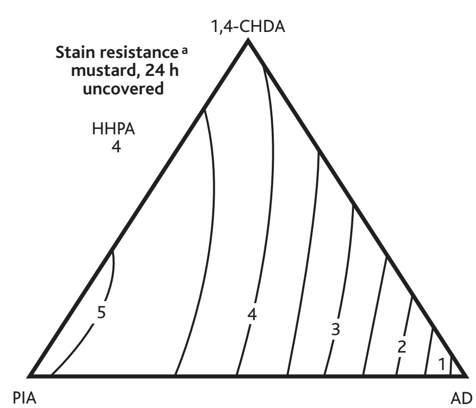
The following battery of stain resistance tests[1]—iodine for 30 minutes and mustard, lipstick, ink, catsup, and grape juice for 24 hours—were conducted on films prepared from the enamel formulation on page 3 (Table 2). All testing was conducted with covered and uncovered stains.

Only the mustard and lipstick results are illustrated. Both Eastman™ 1,4-CHDA and Eastman™ PIA-based resins provided excellent stain resistance trends. Resins based on AD exhibited poor stain resistance. HHPA provides stain resistance properties similar to Eastman 1,4-CHDA and Eastman PIA.









[a]*Scale: 5 = no stain; 4 = slight stain; 3 = moderate stain; 2 = considerable stain; 1 = severe stain*

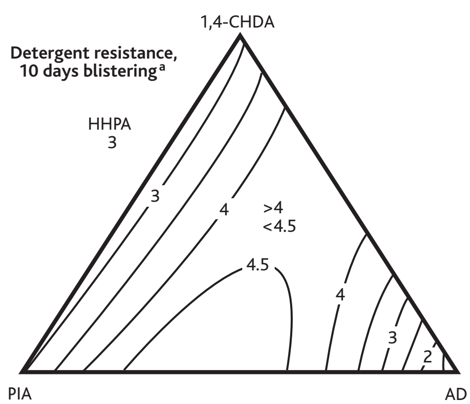
[1]*The stain resistance panels were washed with Dawn™ dishwashing detergent, rinsed with water, and wiped dry before evaluation.*

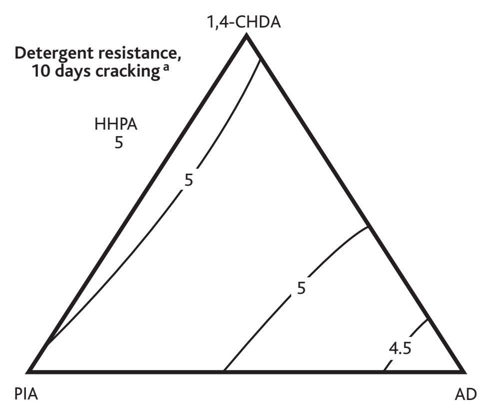
Detergent resistance

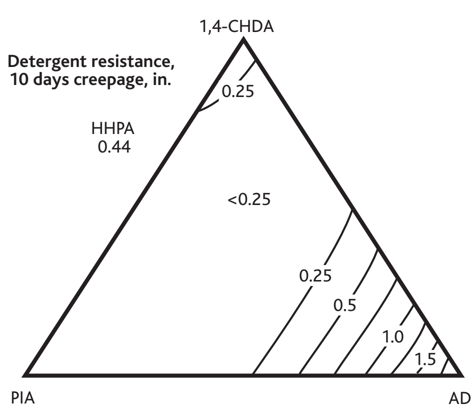
Detergent resistance was determined by immersing scribed and unscribed panels prepared from the resins in a standard detergent solution at 74°C (165°F) for 10 days.

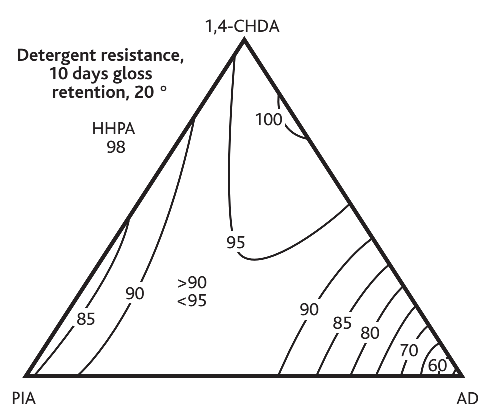
The unscribed panel blistering results show Eastman™ 1,4-CHDA nearly the same as 100% Eastman™ PIA; however, a 1:1 Eastman PIA:AD blend showed some synergy in the blistering results. The cracking and creepage results show Eastman 1,4-CHDA to behave similarly to a 1:1 mix of Eastman PIA:AD. However, cracking and creepage trend worsens as higher AD levels are used as depicted in the following triangles. The same trend can be observed in 20° gloss retention as well. Higher levels of AD in combination with Eastman PIA result in lower 20° gloss retention. Gloss retention trends to a maximum when a 3:1 combination of Eastman 1,4-CHDA:AD is used.

The 60° gloss retention values were omitted because the same trends were followed and the responses were not as sensitive as the 20° gloss retention data. HHPA was similar to Eastman 1,4-CHDA and Eastman PIA testing except for creepage, which trended more towards AD.







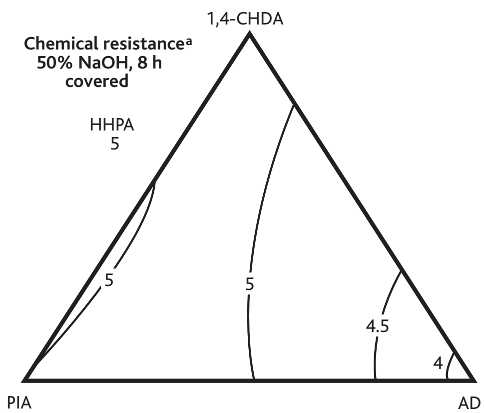


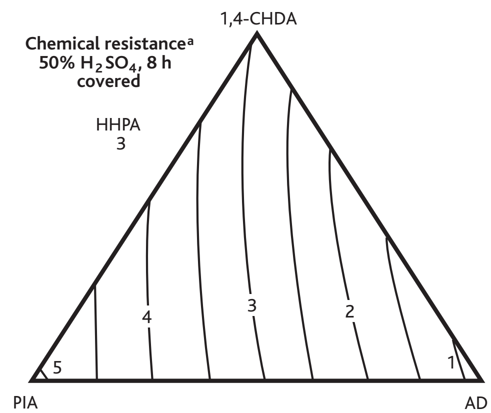
[a]*Scale: 5 = no blistering/cracking; 4 = slight blistering/cracking; 3 = moderate blistering/cracking; 2 = considerable blistering/cracking; 1 = severe blistering/cracking*

Chemical resistance

Chemical resistance[1] was evaluated using 50 weight % solutions of aqueous sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) both covered and uncovered. No significant trend differences were observed between the uncovered and covered test samples. The covered test data is presented in the following triangles.

Under basic conditions, both Eastman™ 1,4-CHDA and Eastman™ PIA performed well. The prepared films were more sensitive to acidic conditions with a 1:1 Eastman PIA:AD blend performing roughly equal to a 100 weight % Eastman 1,4-CHDA resin. Higher AD levels resulted in greater film damage at the pH extremes tested. Acidic conditions were the most detrimental at the high AD level. Again, HHPA behaved much like Eastman 1,4-CHDA and Eastman PIA in this series of tests.



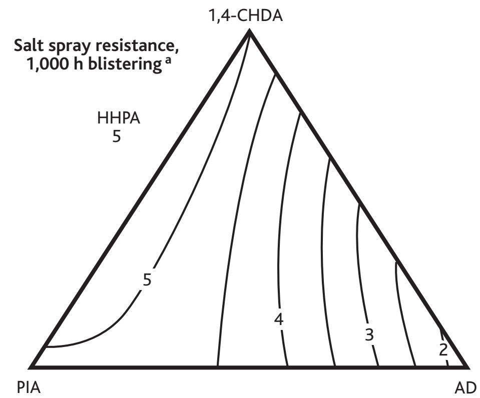


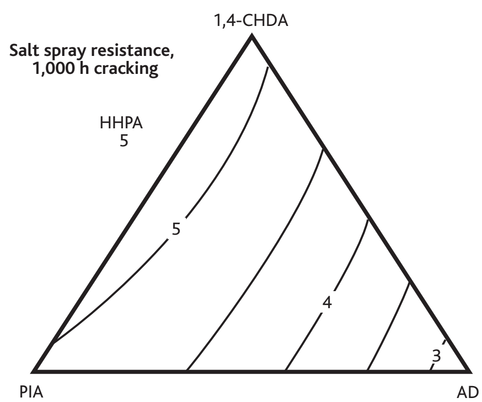
[a]Scale: 5 = resistant; 4 = high resistance; 3 = moderate resistance; 2 = low resistance; 1 = no resistance

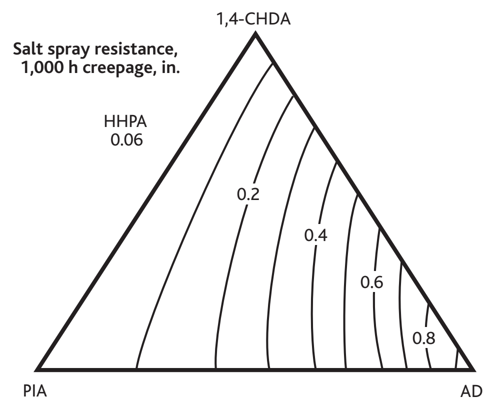
[1]The chemical resistance panels were washed with Dawn™ dishwashing detergent, rinsed with water, and wiped dry before evaluation.

Salt spray resistance

Scribed panels were exposed to 1,000 hours of salt spray using standard methods. Blistering, cracking, and creepage trends benefit from increasing levels of Eastman™ 1,4-CHDA in combination with Eastman™ PIA with a 1:1 Eastman 1,4-CHDA:Eastman PIA blend providing the most favorable trend. Combinations of Eastman 1,4-CHDA:AD do not perform as well with salt spray resistance trending lower with increasing AD levels. HHPA performs much like Eastman 1,4-CHDA in salt spray resistance.







[a]*Scale: 5 = no blistering; 4 = slight blistering; 3 = moderate blistering; 2 = considerable blistering; 1 = severe blistering*

Summary

This statistically designed study was conducted to determine trends and synergies when using combinations of Eastman™ 1,4-CHDA, Eastman™ PIA, and AD in a high-solids resin system based on Eastman TMPD™ glycol. HHPA was included in the study such that the benefits of 1,4 substitution on the cyclohexane ring could be easily identified. Both Eastman 1,4-CHDA and Eastman PIA provide the resin chemist with products that allow specific properties to be maintained without significantly sacrificing other desirable properties. This summary will detail how using Eastman 1,4-CHDA in combination with Eastman PIA supports this statement.

Resins prepared from Eastman PIA:AD blends exhibit positive attributes such as fast processing times, low resin viscosity, low VOC, and good flexibility. These performance points are mainly processing and application derived with the exception of flexibility. However, the ultimate value of a coating to the final customer is determined by how well it performs on the substrate. The aliphatic linear structure of AD weakens properties that affect the useful life of a coating. This is especially true when using AD at higher levels. This decline, whether T_g (glass transition temperature) induced or chemically induced, is quantifiable.

As illustrated in this study, the following coatings performance properties suffer with increasing amounts of AD as compared to comparable levels of Eastman 1,4-CHDA.

Hardness—Films prepared from resins based on Eastman PIA:Eastman 1,4-CHDA blends exhibit a synergistic balance of hardness and flexibility. AD affects hardness more dramatically than Eastman 1,4-CHDA at comparable levels. Resins based on 100 weight % Eastman PIA and HHPA provided the hardest final films. The positive benefits of the 1,4-substitution in Eastman 1,4-CHDA are clearly demonstrated.

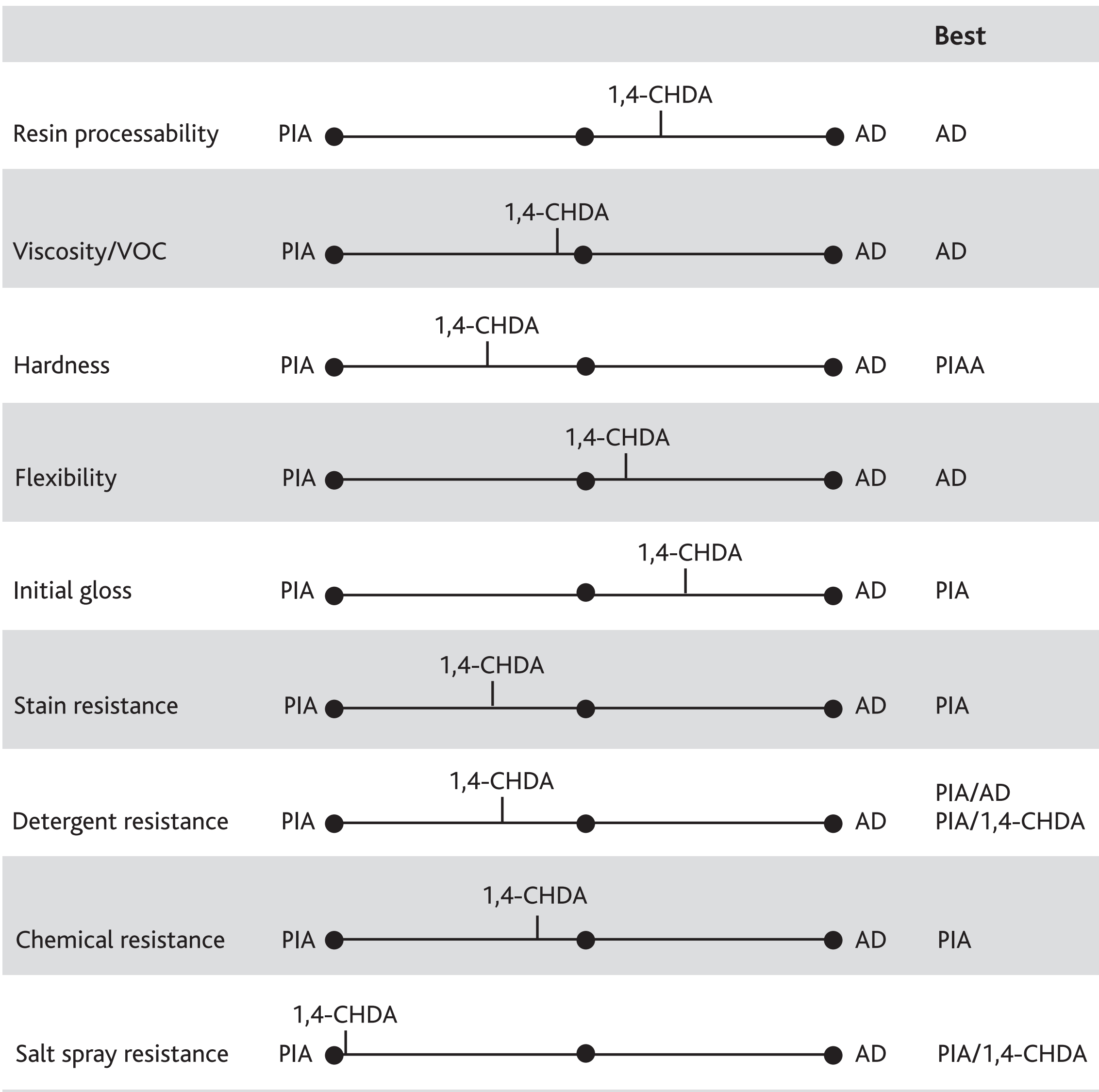
Initial gloss—Eastman PIA affords resins with the highest gloss values in the study. High AD levels adversely affect initial gloss more prominently than comparable Eastman 1,4-CHDA levels. Eastman 1,4-CHDA affects initial gloss similar to AD at low to moderate levels.

Resistance properties—Overall resistance to film degradation is enhanced when using either 100 weight % Eastman™ PIA or combinations of Eastman PIA and Eastman 1,4-CHDA. Resin blends of AD with either Eastman PIA or Eastman 1,4-CHDA generally performed poorer with the exception of detergent resistance blistering which favored a 1:1 PIA:AD. A blend of 1:1:1 Eastman PIA, Eastman 1,4-CHDA, and AD is also compatible. Detergent resistance gloss retention was also an exception with a Eastman 1,4-CHDA:AD blend providing the best results. Resins based on 100 weight % Eastman 1,4-CHDA excelled at salt-spray resistance, outperforming any combination of PIA and AD.

Weatherability is another very important film property that affects the overall durability of a coating. Each end user should generate weathering data specific to end use for any formulation developed based on the results of this study. Generally, resins based exclusively on Eastman PIA weather better than those based on Eastman 1,4-CHDA or AD. However, partial substitution of Eastman PIA with these can still provide acceptable weathering performance especially if the final film contains weathering additives. Hindered amine light stabilizers (HALS) have been shown to provide better enhancement for Eastman PIA resins containing <50 mole % Eastman 1,4-CHDA as opposed to ultraviolet stabilizers (UVAs).

Performance comparison

The graphic below illustrates how Eastman™ 1,4-CHDA performs relative to Eastman™ PIA and AD. The Eastman 1,4-CHDA is unique in that it consistently provides the preferred performance based on most of the properties studied. The best diacid or mixture of diacids for a particular property is listed in the right-hand column for reference.



Related literature

The following list shows publications available from Eastman concerning PIA and 1,4-CHDA. They range from basic data sheets to suggested starting point formulations for specific applications. A number of these publications are available online at www.eastman.com.

Number	Title	Description
Eastman™ PIA		
N-353	Eastman™ purified isophthalic acid	General data sheet
N-307	Eastman™ resin intermediates and their performance characteristics	Brief overview of Eastman products for the resins industry
Eastman™ 1,4-CHDA		
N-337	Eastman™ 1,4-CHDA (high purity)	General data sheet
N-321	High-solids polyester resins for appliances and general metal coatings based on Eastman™ 1,4-CHDA and Eastman NPG™ glycol	Starting point resin formulations, coatings formulation, and subsequent final film properties
N-330	Appliance coil coating based on Eastman™ 1,4-CHDA and Eastman™ CHDM	Specific resin formulation, coating formulation, and final film properties
N-327	Improved coil coating performance with Eastman™ 1,4-CHDA	Resin and film benefits of using Eastman 1,4-CHDA in coil coatings

Additional information

Eastman Chemical Company's website, www.eastman.com, contains a wealth of additional information for both Eastman™ 1,4-CHDA and Eastman™ PIA as well as information for other Eastman products used in the resins industry. Specific questions concerning Eastman resin intermediates can be submitted to Technical Services via the web.

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