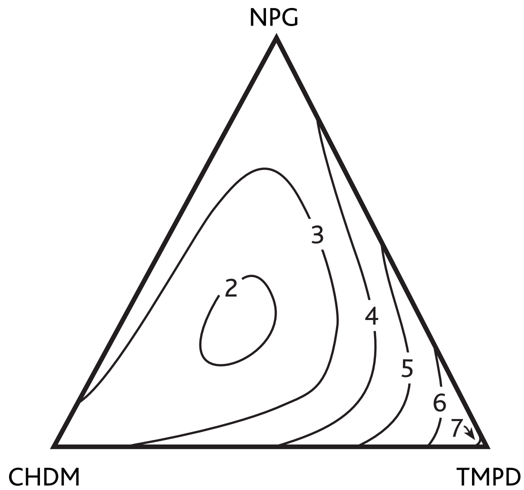
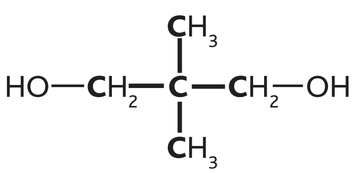
Eastman™ triangle glycol study



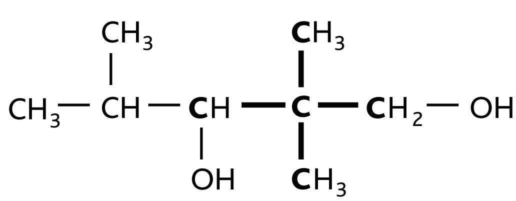
Neopentyl family

NPG glycol



IUPAC 2,2-dimethyl-1,3-propanediol

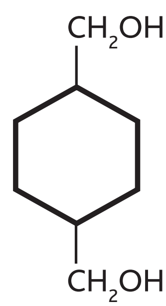
TMPD glycol



IUPAC 2,2,4-trimethyl-1,3-pentanediol

Cycloaliphatic Family

CHDM glycol



IUPAC 1,4-cyclohexanedimethanol

Introduction

A key application for our glycols is in saturated polyesters for coatings. The influence of Eastman NPG™, Eastman TMPD™, and Eastman™ CHDM glycols on resin and coating properties was investigated through the use of a statistically designed study. The results are described in this publication.

For many years, Eastman has described the performance offered by its line of polyester intermediates through their structure/property relationship.[1] A basic structural comparison of these 3 glycols is shown in Table 1.

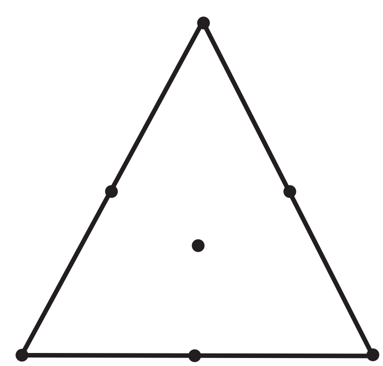
Table 1 **Structural comparison of Eastman™ glycols**

	NPG	TMPD	CHDM
Structure type	Aliphatic	Aliphatic	Cycloaliphatic
Hydroxyl types	2 Primary	1 Primary 1 Secondary	2 Primary
Hydroxyl orientation	1,3	1,3	1,6
Steric hindrance	2 Me	2 Me 1 i-Pr	1 Cyclohexane ring

Experimental details

The method of investigation chosen to study these glycols was a statistically designed mixture experiment.[2–4] The study was based on a typical high-solids resin composition.[5] The design of the experiment is shown in Figure 1 with a dot representing each resin included in the study. A dot at the corner of the triangle indicates 100% usage of the glycol in the resin, while a dot at the midpoint of a triangle leg represents 1:1 molar blend of those two glycols. The dot at the center of the triangle means equal molar amounts (1:1:1) of all 3 glycols were used in the resin. The total high-solids resin compositions and resin property boundaries are described in Table 2. All resins were cooked to similar acid numbers, molecular weights, and hydroxyl numbers (see Table 3).

Figure 1
Experimental design



[1]*Eastman Publication N-307*
[2]*Eastman Publication N-335*
[3]*Eastman Publication N-323*
[4]*Eastman Publication N-327*
[5]*Eastman Publication N-362*

Table 2 Resin compositions and properties

			Moles
Resin compositions	Glycols		2.97
	Trimethylolpropane[a]		0.27
	Eastman™ 1,4-CHDA		0.67
	Eastman™ purified isophthalic acid (PIA)		0.67
	Adipic acid		0.67
Resin properties	Final acid number, mg KOH/g resin	2–8	
	Molecular weight (Mn by GPC)	700–900	
	Hydroxyl number, mg KOH/g resin	120–150	
	Wt% solids in xylene	75–80	

[a]*Two-stage addition of trimethylolpropane*

Table 3 Resin summary

Resin composition			Resin properties			
Eastman NPG™ glycol	Eastman TMPD™ glycol	Eastman CHDM™ glycol	Mn	OH#	AN	T_g°C
100	0	0	750	141	2	–18
50	50	0	851	128	4	–11
50	0	50	673	146	5	–4
33	33	33	693	141	6	–8
0	100	0	755	131	8	–25
0	50	50	804	128	6	–3
0	0	100	725	134	8	–2

The resulting 7 resins were formulated into typical white enamels per Table 4. Additional solvent blend was added to each enamel to obtain a viscosity of 29–30 seconds (#4 Ford cup). The enamels were sprayed onto Bonderite™ 37 pretreated 20-gauge, cold-rolled steel test panels and were baked to a similar degree of cure as measured by MEK double rubs to mar (range = 110–180) to obtain a cured film thickness of 1.7–2.1 mils.

Table 4 Enamel formulation

Ingredients	Wt%
Polyester resin (calculated 85 wt% 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 wt% N.V.)	0.4
Fluorad™ FC-430 flow control additive[c] (20 wt% N.V.)	0.5
Solvent blend[d]	11.6
	100.0
Pigment:binder weight ratio	40:60
Polyester:melamine weight ratio	75:25

[a]*Cytec*
[b]*DuPont*
[c]*3M Company*
[d]*Eastman™ MAK/Eastman™ EEP* n-*butyl alcohol in a weight ratio of 4:1:1*

Results interpretation and index

The results obtained through the determination of various resin and enamel properties were used to generate numerous contour maps. Regression analysis was used to interpret the data. An example of one such contour map is shown in Figure 2.

One additional and very desirable piece of information can be gained through the use of statistically designed mixture experiments—the occurrence of synergism and/or antagonism. **Synergism** occurs when one obtains better-than-expected results when combining components. **Antagonism** occurs when one obtains worse-than-expected results when combining components. Synergism is what every experimentalist hopes to obtain but can never predict. The symbols (used as superscripts) shown in the following are used throughout this text to indicate the presence of synergism or antagonism for a given performance property. Look for these important features.

Symbol key

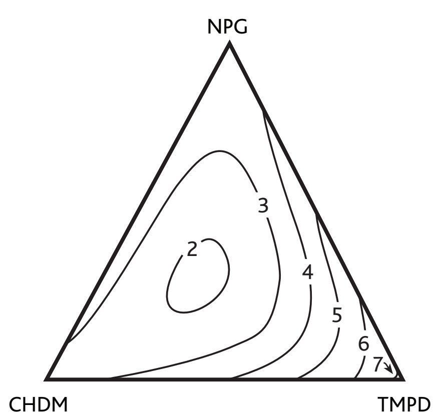
+/S = Synergism
–/A = Antagonism

Desired **Undesired**

C = CHDM N = NPG T = TMPD

Figure 2

Process time in hours



The trends generated from this information will be shown on a horizontal line with the desired performance on the left and the undesired performance on the right. The performance of each glycol is designated by the first letter of its name (i.e., N for Eastman NPG™ glycol). The overall performance is obtained by averaging all the evaluations in the given category. The purpose of this form of data presentation is to compare the performance of one glycol to another and not to indicate that one glycol is "good" while another is "bad." It is suggested that Eastman NPG™ glycol be used as a reference point because most of the coatings industry is familiar with its performance in various applications. Users should take careful note of the range of performance differences and determine for themselves whether the range is wide enough to justify changing the resin glycol composition for a specific application. The performance categories investigated are shown in Table 5.

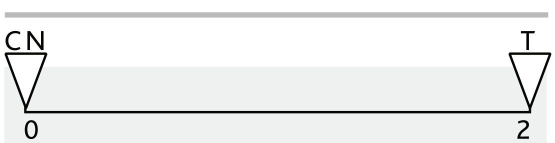
Table 5 **Performance**

Performance property	Page
Processability	5
Cure response	6
Volatile Organic Compound (VOC)	6
Viscosity	7
Hardness	8
Flexibility	9
Stain resistance	10
Detergent resistance	11
Cleveland humidity	12
Salt spray	13
Summary	13

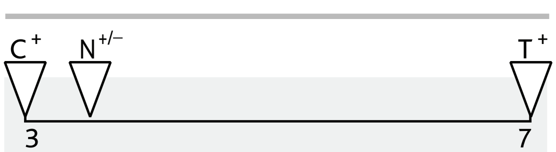
Processability

The cycloaliphatic structure of Eastman™ CHDM appears to offer increased reactivity of its primary hydroxyl groups relative to the primary hydroxyl groups of Eastman NPG™ glycol. The cyclohexane ring must minimize steric interference of the hydroxyl groups—making them readily accessible for reaction. The combination of one secondary hydroxyl group and a high degree of steric shielding of the hydroxyls significantly decreases the reaction rate of Eastman TMPD™ glycol relative to other glycols.

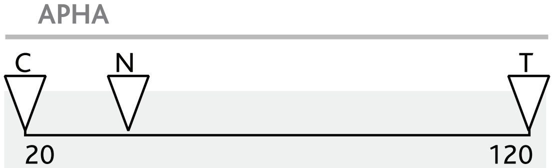
Organic distillate[a] water-insoluble wt% loss



Process time, h

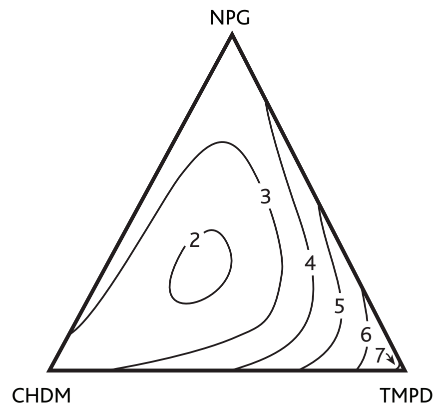


Resin color[a] APHA

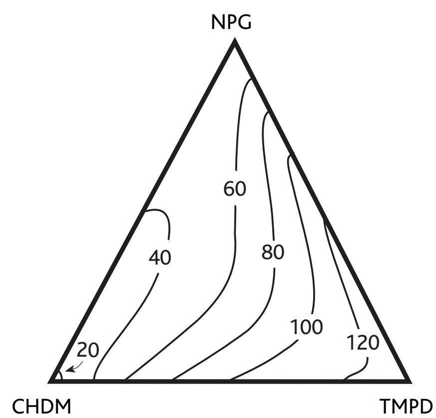


Overall

Process time, h



Resin color APHA



[a] *Eastman TMPD™ can dehydrate during resin synthesis giving small amounts of water-insoluble rearrangement products in the distillate. These rearrangement products also add to resin color.*

Note: Symbol definition key on page 4.

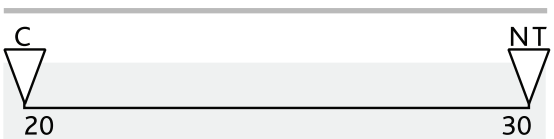
Cure response

The cycloaliphatic structure of Eastman™ CHDM with its readily accessible hydroxyl groups clearly provides for a rapid cure response with crosslinking resins as compared to the other glycols. This is consistent with the processability performance definition (page 4). Surprisingly, Eastman TMPD™ glycol shows no significantly slower cure response as compared to Eastman NPG™ glycol in this study. Note that a 1:1 combination of CHDM and TMPD shows a significant decrease in cure time.

VOC

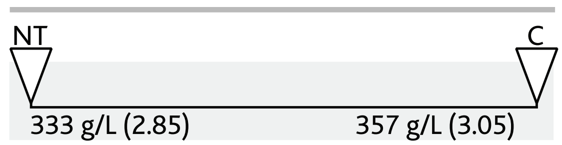
No significant difference in volatile organic compound (VOC) was observed between Eastman NPG™ and Eastman TMPD™ glycols; however, it has been demonstrated through countless commercial resins that TMPD glycol yields lower VOC coatings, due to its bulky asymmetrical structure. The cycloaliphatic structure of Eastman™ CHDM provides for close packing of the polymer chains and a high degree of hydrogen bonding between chains. This results in higher solution viscosities of the resins and VOCs of the coatings.

Cure time min at 163°C (325°F)



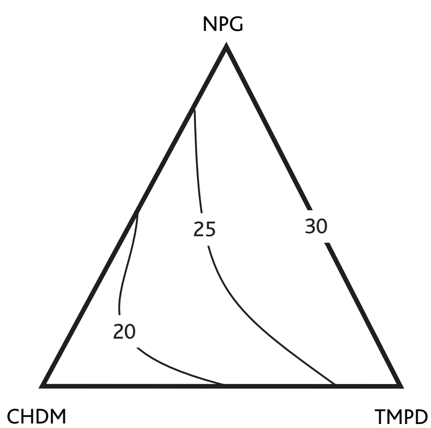
Note: Symbol definition key on page 4.

VOC at 149°C (300°F) for 20 min, g/L (lb/gal)

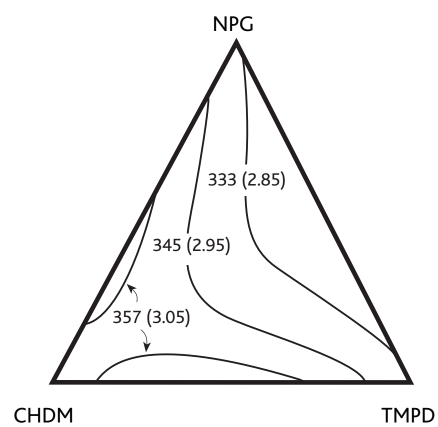


Note: Symbol definition key on page 4.

Cure time min at 163°C (325°F)



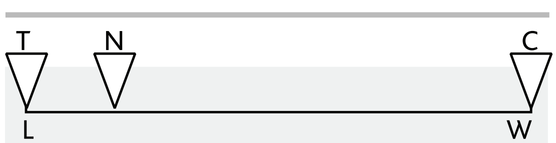
VOC at 149°C (300°F) for 20 min, g/L (lb/gal)



Viscosity

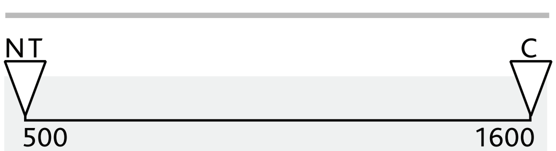
Eastman NPG™ and Eastman TMPD™ glycols gave very similar results in terms of both neat and solution viscosities of the resins. Look at each performance definition separately to obtain a greater degree of differentiation of these glycols. The 1,4-cycloaliphatic structure of Eastman™ CHDM (as compared to the aliphatic structure of the other glycols) gave significantly higher viscosity resins.

Gardner at 70% solids



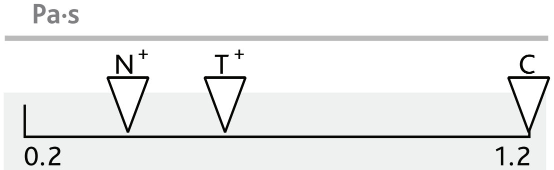
Brookfield at 70% solids

mPa·s



ICI at 100°C

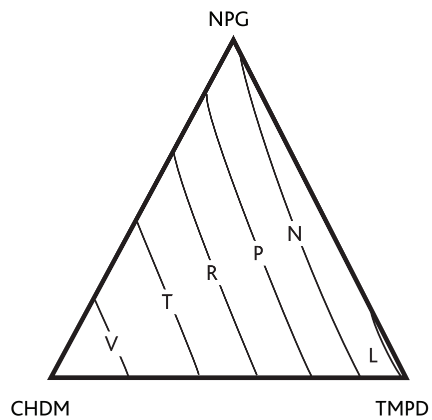
Pa·s



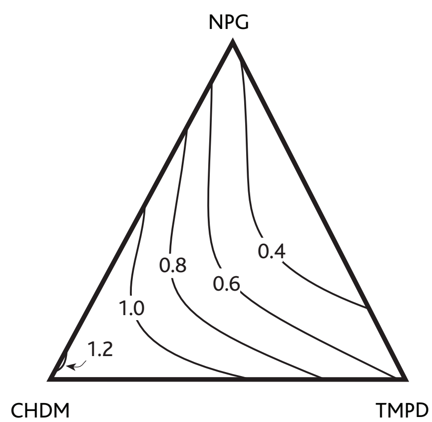
Overall

Note: Symbol definition key on page 4.

Gardner viscosity at 70 wt% solids



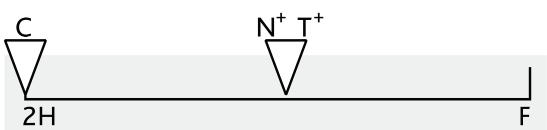
ICI viscosity at 100°C, Pa·s



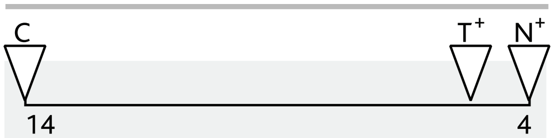
Hardness

The 1,4-orientation about its cyclohexane ring results in Eastman™ CHDM giving the hardest film of the glycols evaluated in this study. Note the opportunity for improvement (synergism) by combining Eastman NPG™ and Eastman TMPD™ glycols properly.

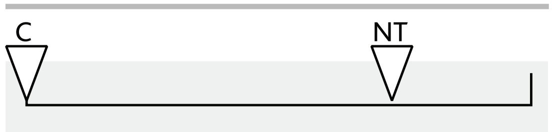
Pencil to mar



Tukon knoops

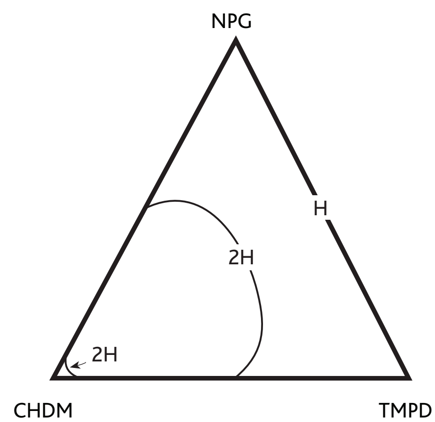


Overall

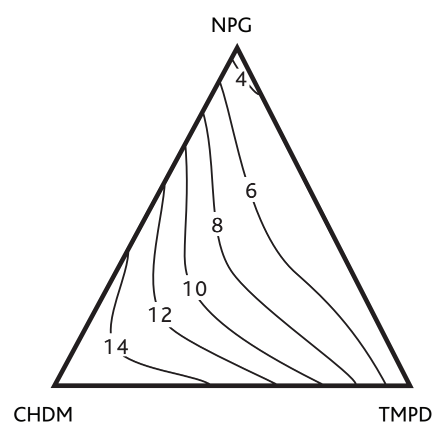


Note: Symbol definition key on page 4.

Pencil hardness to mar



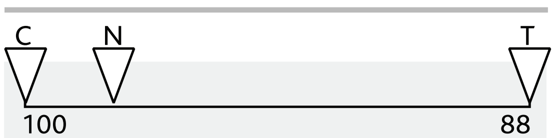
Tukon hardness knoops



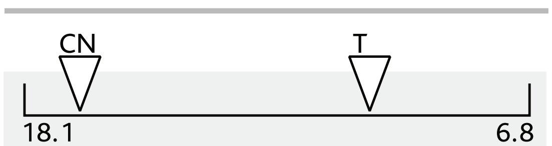
Flexibility

Eastman TMPD™ glycol is clearly the least flexible of the glycols evaluated in this study. Note the synergism in the reverse impact resistance evaluation.

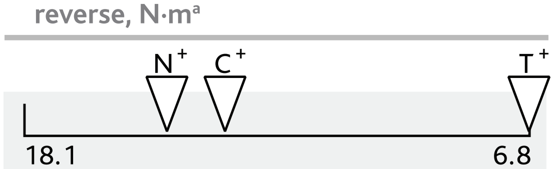
Conical Mandrel % pass



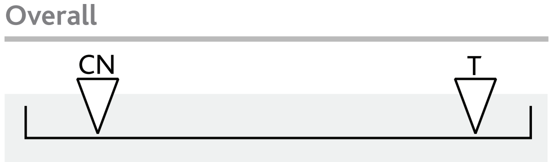
Impact resistance forward, N·m[a]



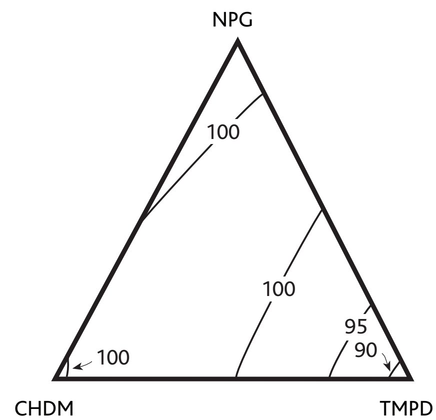
Impact resistance reverse, N·m[a]



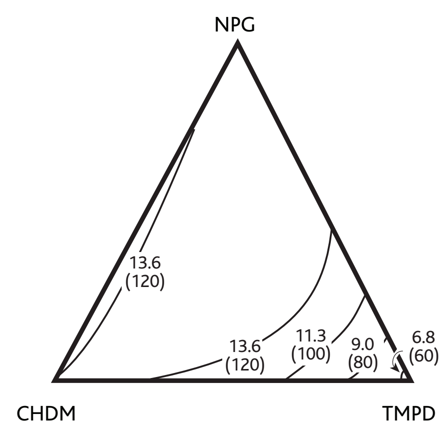
Overall



Conical Mandrel % pass



Impact resistance reverse, N·m (in.-lb)



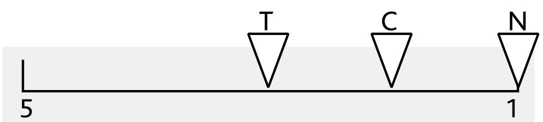
[a]*Newton meter*

Note: Symbol definition key on page 4.

Stain resistance

A wide variety of results were obtained from one stain test to another. This resulted in a bunching in the overall performance. It is suggested that the formulator look at the specific test that matches the application.

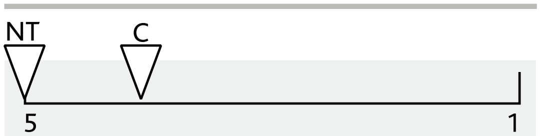
Iodine, 30 min covered



Lipstick, 24 h covered

Mustard, 24 h covered

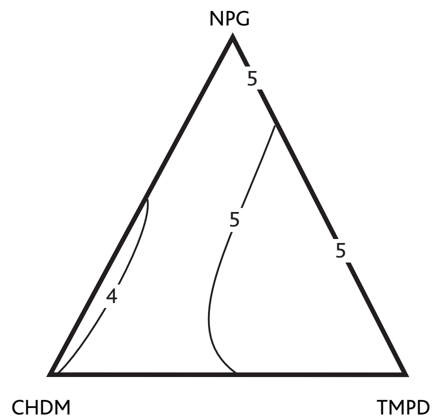
Mustard, 24 h uncovered



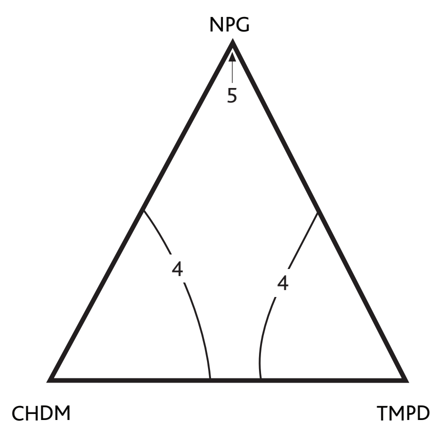
Overall

Note: Symbol definition key on page 4.

Stain resistance mustard, 24 h, uncovered



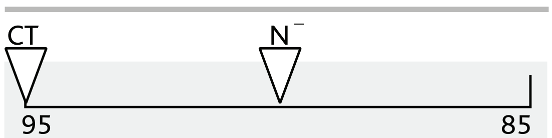
Stain resistance lipstick, 24 h, covered



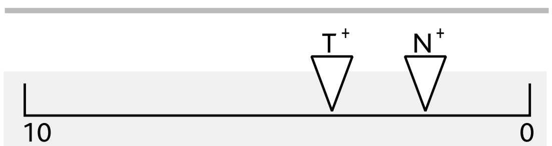
Detergent resistance

The five-day detergent resistance[1] results show that Eastman™ CHDM, followed by Eastman TMPD™ glycol, provides films with the best overall performance of the glycols evaluated in this study. The higher T_g of CHDM systems and the steric shielding of TMPD glycol are possible reasons for these results.

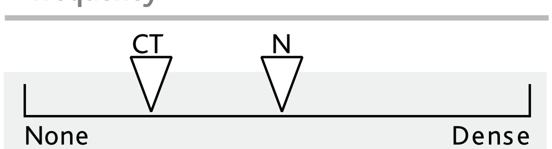
60° Gloss retention, %



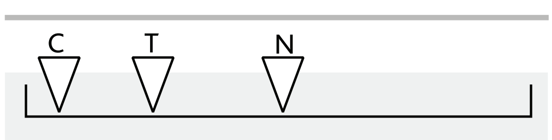
Blistering[a] size



Blistering[a] frequency



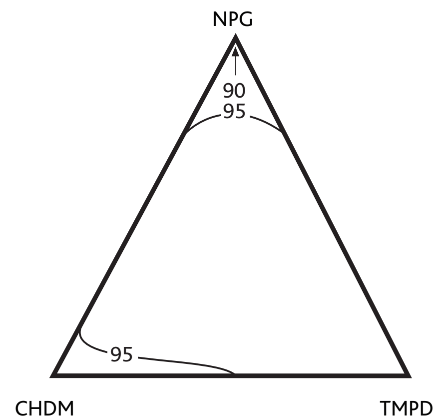
Overall



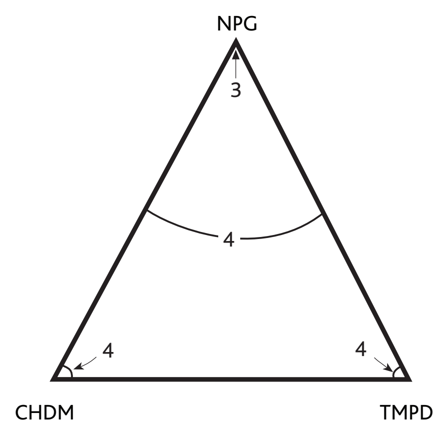
[a]*ASTM D174*

Note: Symbol definition key on page 4.

Detergent resistance 60° gloss retention, %



Detergent resistance blistering, frequency

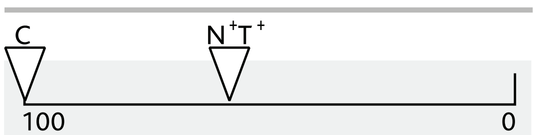


[1]*ASTM D2248-73*

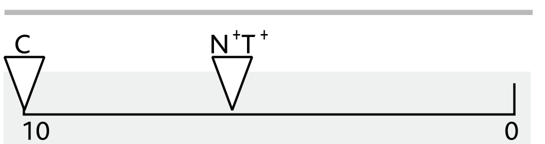
Cleveland humidity

The results for the Cleveland humidity test[1] (2000 h at 60°C [140°F]) show that cycloaliphatic Eastman™ CHDM clearly outperforms the aliphatic glycols (NPG and TMPD glycols). This strongly suggests the higher T_g (averaging 15°C higher compared to resins containing no CHDM) of the cycloaliphatic containing resins is a very important factor in this performance characteristic.

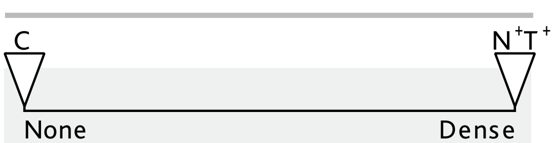
20° Gloss retention, %



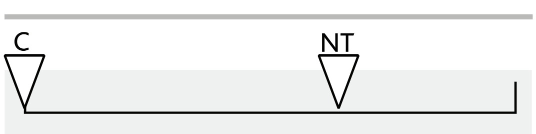
Blistering[a] size



Blistering[a] frequency



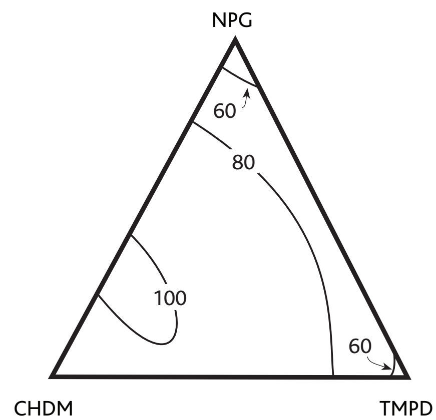
Overall



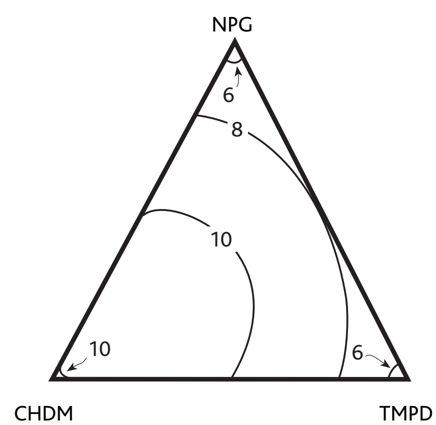
[a]*ASTM D174*

Note: Symbol definition key on page 4.

Cleveland humidity 20° gloss retention, %



Cleveland humidity blistering, size

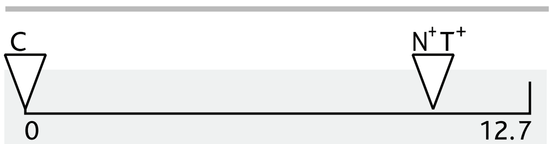


[1]*ASTM D4585*

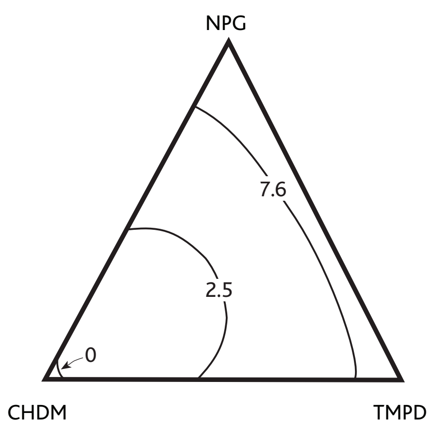
Salt spray

The 1000-hour salt spray test[1] results show that the cycloaliphatic structure of Eastman™ CHDM gives films with the best resistance to creepage from the scribe.

Creepage
mm



Salt spray
Creepage, mm



[1]ASTM B117-64
Note: Symbol definition key on page 4.

Summary

The trends shown following the summary can be used by the resin chemist to make the best "first choice" of glycols to be selected for a new resin or resin improvement. This information should better define the performance properties imparted to resins and coatings by these 5 glycols (relative to each other). Understanding the structure/property relationships of these glycols makes it easier to design resins for specific end-use applications.

Coated samples were subjected to accelerated weathering via EMMAQUA (24 months), QUV-A (2300 hours), and natural weathering in Florida (5° South, Black Box, 12 months). Results were not statistically significant and therefore are not included here.

The following are some generalized statements about each of the Eastman™ glycols:

Eastman NPG™ glycol: A well-known industry standard for many applications (appliance, coil, powder, etc.); very good overall performance; used as the key reference point with which the other glycols in this study were compared.

Eastman TMPD™ glycol: First choice commercially for highest-solids applications due to bulky structure; steric shielding of the hydroxyl groups provides for good hydrolytic stability and stain resistance; slowest to process; poor hardness/flexibility ratio.

Eastman™ CHDM: Only Eastman glycol with the unique cycloaliphatic structure yields higher T_g resins than aliphatic glycol-based resins; offers good salt spray, Cleveland humidity and detergent resistance; cycloaliphatic structure gives best hardness/flexibility ratio; fastest processing and curing glycol; main disadvantages are high solution viscosity and VOC.

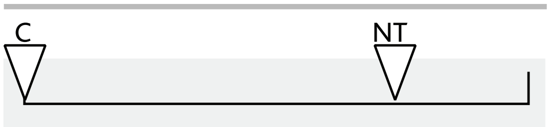
Processability[S/A]

Cure response

VOC

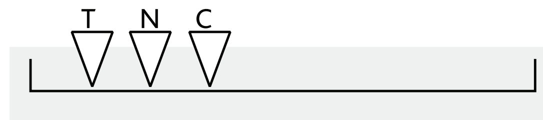
Viscosity

Hardness[S]

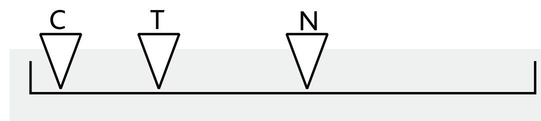


Flexibility[S]

Stain resistance

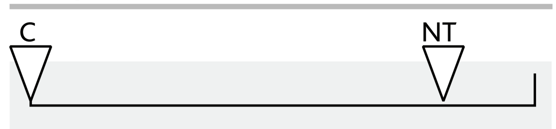


Detergent resistance[S/A]



Cleveland humidity[S]

Salt spray[S]



Note: Symbol definition key on page 4.

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