Application Data

MPDiol® Glycol

MPDiol Polyester Polyols for Urethane Coatings

General Information

MPDiol has the reactivity characteristics of diprimary diols but it has the favorable handling characteristics of many of the branched diols. Polyol branching makes polymers resulting from these less likely to crystallize upon sitting, increasing the shelf life of the paint. Polyurethanes made from MPDiol exhibit hybrid properties, somewhere between a long chain and branched polymer. It exhibits good curing, flexibility, and toughness as compared to commonly used diols.

Key Features and Benefits

Faster Esterification Rates: Esterification rates for the same acid value are up to 30% faster with MPDiol. The diprimary nature of MPDiol ensures better reactivity with diacids.

Non-crystallizing Coatings: The unsymmetrical nature of the MPDiol molecule prevents close packing of the resin polymer chains. This is evidenced by longer shelf life of the product without hazing, cloudiness, or particulates developing in the solutions.

Fast Curing: The resulting polyester polyol is primary in nature and tends to react quickly with diisocyanates. MPDiol exhibits similar reactivity to that of 1,3-propandiol and the resulting films show performance equal to commonly used polyols.

Polyester Polyol Synthesis and Propert Benefits

Preparation of the polyester polyols consisted of an excess of glycol, a small amount of trimethylolpropane, and corresponding diacids cook without the use of a catalyst. The esterification was performed at 213 °C. Several polyester polyols were synthesized using this method. The make up of each resin is summarized in Table 1. Diols included in the study were primary and secondary. The primaries were used as direct comparisons of processing reactivity. Secondary diols were used as structural and spatial arrangement comparisons. The differences in the amounts used in the synthesis of diprimary versus primary/secondary polyols stemmed from past experiences in making propylene glycol (PG) based polyesters. Secondary alcohols react slower than primary alcohol; higher temperatures can solve the reactivity problem but a greater amount of diol is necessary in order to compensate for evaporation. Use of excess glycol ensured that the polyols synthesized were of comparable acid numbers. 1,4-Butane diol (1,4-BDO) and trimethylpentane diol (TMPG) yielded lower hydroxyl polyols because of considerable side reactions. Gel permeation chromatography (GPC) results support this side reaction theory yielding broad bands suggestive of a wider range of molecular weight distributions. The increased amount of side product shows up as tailing in the GPC and these higher molecular weight products increase the final resin viscosity. Properties of the polyols and the nature of the diol are summarized in Table 2.

Resin Components	*Diprimary Diols moles*	*Primary/Secondary Diols*
Diol	4.30	4.51
Isophthalic Acid	2.00	2.00
Adipic Acid	2.00	2.00
Trimethylolpropane	0.70	0.70

Table 1. Generic polyester polyol synthesis and resin composition used for comparative testing of commonly used primary and primary/secondary hydroxyl diols and MPDiol.

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Diol Component	*Hydroxyl Number mg KOH/g*	*Acid Number mg KOH/g*	*Mn*	*Mw*	*Mw/Mn*
MPDiol	128	5.3	1260	2540	2.02
Ethylene glycol	162	6.2	920	2010	2.18
1,3-Propane diol	150	6.3	1100	2120	1.94
1,4-Butane diol	84	11	1840	4780	2.60
1,6-Hexane diol	131	6.8	1370	2620	1.91
Neopentyl glycol	130	8.8	1160	2200	1.89
Propylene glycol	132	6.6	920	1880	2.03
1,3-Butane diol	148	6.2	1050	2070	1.96
Trimethylpentane diol	94	11.0	1350	5240	3.87

Table 2. Properties of resulting polyester polyols from several primary and primary/secondary hydroxyl glycols as compared to MPDiol

Substituting MPDiol one to one in this study provided a means for direct comparison and quantification of the structure reactivity correlation between MPDiol and other diols with similar characteristics. We measured the effects of diol selection on the synthesis rate and properties of the polyester polyol. The reactivity profiles of the diols were plotted to compare the reactivity of MPDiol to these. (See Figure 1) In this plot the increase in curvature is indicative of an increase in rate. The results suggest that ethylene glycol reacts the fastest under the esterification conditions followed by MPDiol and 1,3-propanediol. Even the branched nature of MPDiol does not interfere with its reactivity as evidenced by it reacting faster than linear 1,4-BDO and much faster than NPG.

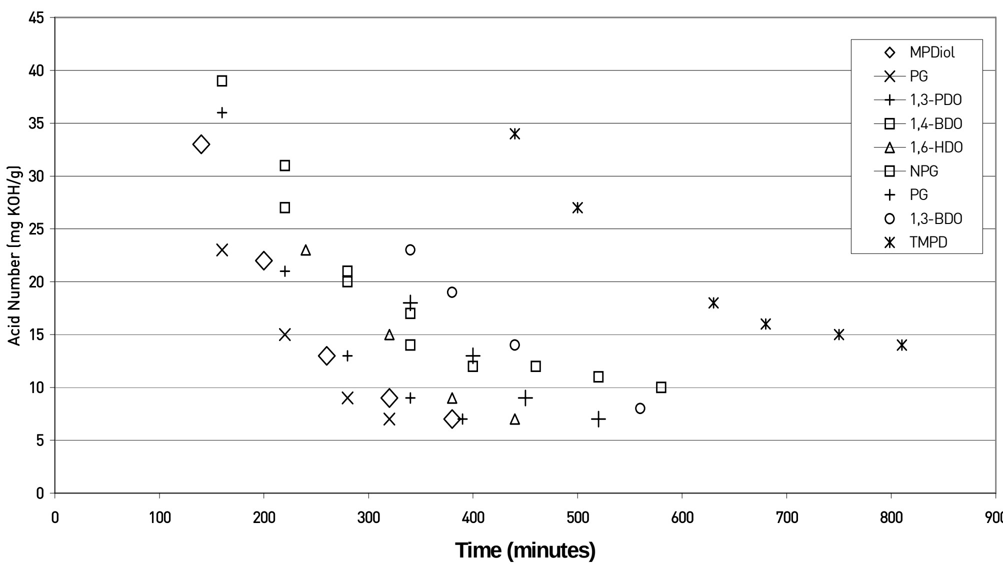

Figure 1. Polyesterification reactivity profile of commonly used primary and primary/secondary hydroxyl glycols plotted against MPDiol glycol for comparison.

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A solvent compatibility or tendency for crystallize test was performed on the polyester polyols. Crystallization is evidenced by a cloudy, hazy or sometimes particulate in the resin. Over a period of three weeks only the MPDiol, 1,6-HDO, and all of the secondary/primary diol based polyesters remained clear. The results support the belief that branched polyols hinder close packing of the polyester chains and in this way inhibiting crystallization. A summary of the results is shown in Table 3. MPDiol is an attractive intermediate for use in polyester synthesis when combined with its reactivity and inherent compatibility with organic solvents it can reduce processing costs and increase shelf life of the final product.

Diol Component	*Gardner-Holt Viscosity*	*Gardner Color*	*Clarity after 3 weeks*
MPDiol	Z-4	1	Clear
Ethylene glycol	Z-5	1	Cloudy
1,3-Propane diol	Z-3	2	Hazy
1,4-Butane diol	Z-6	1	Cloudy
1,6-Hexane diol	Z-1	1	Clear
Neopentyl glycol	Z-6	1	Hazy
Propylene glycol	Z-5	1	Clear
1,3-Butane diol	Z-2	1	Clear
Trimethylpentane diol	Z-8	4	Clear

Table 3. Three-week stability testing using 90% polyester polyol solids in 1:1 methyl ethyl ketone and propylene glycol methyl ether blend on a variety of polyester polyols including a MPDiol glycol based polyester.

Polyurethane Polymers

Clear coat, two-pack aliphatic polyurethane coatings were prepared using the basic formulation shown in Table 4. Curing conditions were kept constant so that a direct comparison could be made between polyols. Methylethyl ketone (MEK) double rub performance of the films showed that these cured completely. The films showed good flexibility and resilience as well as toughness and hardness. The performance data suggests that the MPDiol based urethanes behave similar to 1,3-propandiol (1,3-PDO) since it cures as fast as 1,3-PDO and demonstrates comparable hardness. On closer inspection it is really a hybrid since it is a primary hydroxyl with a branched backbone. The film shows a high pencil hardness signifying it is as hard as a conventional branched system. As expected softer more resilient films than expected were obtained commensurate with conventional long chain polyols and evidenced by its sward hardness value.

Summary

MPDiol shows to be a viable alternative diol for the synthesis of polyester polyols. It affords colorless polyols while allowing for processing temperature latitudes that other diols cannot afford. The process time is shorter and urethane resin synthesis faster than similar diols. The resulting coating performance is comparable to commonly used diols and more stable in organic solutions than many of the diprimary diol commonly used for these applications. It is expected that the films should yield a weatherable and humidity stable coating. (See Application Data sheet titled "Weatherability of Melamine Cured Polyesters").

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Formulation	*Weight (gm)*		
Part A			
Resin Solution	40.0		
ARCOSOLV® PM Acetate[1]	5.0		
Methyl Ethyl Ketone	5.0		
Xylenes	5.0		
FC- 430 (Flow Control Additive)[2]	0.28		
T-12 (Catalyst)[3]	0.20		
Part B			
Desmodur® N-3390 (90% NVM)[4]	NCO:OH 1.10: 1.00		
Polyol	*Properties of Polyurethane Film[5]*		
	MEK 2X RUBS	*Pencil Hardness*	*Sward Hardness*
Primary Diols			
MPDiol	>100	2H	8
EG	>100	3H	20
1,3-PDO	>100	2H	8
1,4-BDO	>100	H	2
1,6-HDO	>100	F	2
NPG	>100	H	32
Secondary Diols			
PG	>100	F	24
1,3-BDO	>100	H	16
TMPD	>100	H	22

Table 4. Formulation and film properties for several primary and primary/secondary hydroxyl based polyester polyols used in formulating polyurethane coatings.

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2412-V3-0304
Supersedes 2412-V2-0303