Application Data

MPDIOL Glycol

MPDIOL Glycol in Polyester Resins for
Low-VOC Waterborne Can or Coil Coatings

General Information

MPDIOL glycol (2-methyl-1,3-propanediol) is a aliphatic diol with unique properties and high performance. Its branched structure imparts flexibility in polyesters and lowers their viscosity. These features make *MPDIOL* glycol particularly useful for the production of polyesters for can and coil coatings, where a combination of flexibility, toughness, and weatherability is required. This bulletin describes the preparation and use of *MPDIOL* glycol in low-VOC (<2.0 lbs/gallon) waterborne coatings suitable for can or coil.

Key Features and Benefits

Ease of Handling: Unlike some other glycols, *MPDIOL* glycol is a low viscosity liquid well below ambient temperature and is supplied water-free. This facilitates reactor loading, improves production rates, especially with relatively insoluble diacids such as terephthalic acid, and reactor unloading. *MPDIOL* glycol can be easily pumped into the reactor and help solvate solid acids and anhydrides. This results in faster esterification, lower production costs, and lower viscosity polyesters.

High Reactivity: Due to its primary hydroxyl functionality and high boiling point, *MPDIOL* glycol reacts faster with diacids than diols with secondary hydroxyl groups or low boiling points. Using *MPDIOL* glycol in the synthesis of polyesters reduces cycle times and cost**.** In polyester formulations, it also allows for greater use of terephthalic acid and phthalic anhydride, two inexpensive raw materials.

Toughness and Durability: The branched structure of *MPDIOL* glycol imparts flexibility to polyesters and lowers their viscosity. These features make *MPDIOL* glycol particularly useful for the production of polyesters for can and coil coatings where a combination of flexibility, hardness, water resistance and weatherability is required.

Properties

Chemical Name	2-Methyl-1,3-propanediol
CAS Number	2163-42-0
Molecular Weight, grams/mole	90.1
Hydroxyl Functionality	Both primary
Minimum Purity by Weight	98%
Viscosity (Brookfield @25°C)	174 cps
Melting Point	- 54°C
Boiling Point (@760 mm Hg)	212°C
Flash Point (Closed Cup)	127°C
Density	1.01 g/cm^3 @ 20°C
Hydroxyl Number (mg KOH/gram)	1,246
Equivalent Weight	45.1
Vapor Pressure @100°C	4.3 mm Hg
Appearance	Clear liquid
Color, (APHA)	<10

These are typical values, not sales specifications.

Polyester Synthesis

Polyesters are prepared by condensation of diacids or anhydrides and diols. Several factors can affect resin cost:

- Raw materials
- Cycle time
- Energy requirements
- Batch yields

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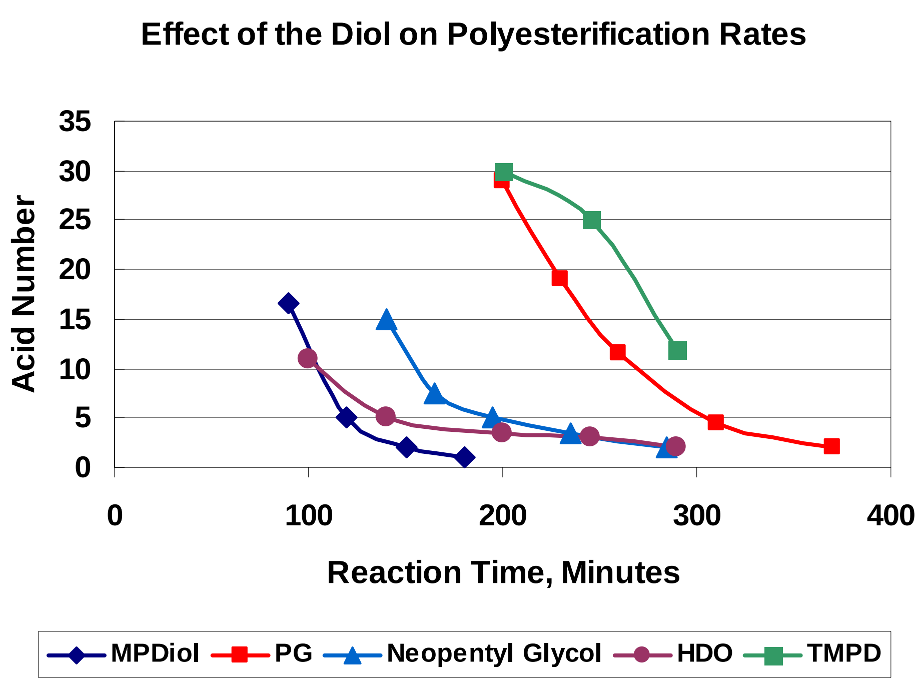
Proper selection of raw materials is the most important because it affects not only the cost of the polyester but also its performance. Both diols and diacids can affect the polymerization kinetics, cycle times, and, consequently, cost. Due to its primary hydroxyl functionality and high boiling point, *MPDIOL* glycol reacts faster than diols with secondary hydroxyl groups or low boiling points. This is illustrated by the graph below, which shows the drop in acid number for several diol/adipates. Acid number is a common measure of the degree of esterification. The boiling points, melting points, and type of hydroxyl functionality of

	PG	*MPDIOL* glycol	BDO	Neopentyl	HDO
Melting Point, °C	< - 60	- 54	16	125	43
Boiling Point, °C	189	212	235	206	250
Functionality	1°& 2°	1°	1°	1°	1°



common diols are listed below:

Diol Features	**Resin Benefits**
Primary functionality, high boiling point	Rapid Esterification
Liquid well below ambient temperature	Easy handling
Asymmetric branched structure	Improved flexibility Improved storage stability Lower VOCs Low-viscosity polyesters

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Polyesters for Can and Coil Coatings

Performance requirements for can and coil coatings are similar. They apply to both the formulation and the film properties. Formulations must be storage stable, have low VOC contents, and be inexpensive. Coil and can coatings are applied to flat metal stock, heat cured, and the coated metal then formed into various shapes. Typical applications include aluminum siding, gutters, truck trailers, appliances, and metal containers.

Because the parts are coated before they are formed, flexibility and adhesion are critical performance requirements for these coatings. Typical requirements are listed below:

- Zero T-bend flexibility
- Excellent adhesion
- Hardness and abrasion resistance
- Weatherability for coil
- Color retention under retort or pasteurization conditions for can
- Stain, detergent and corrosion resistance

Because of stringent weatherability requirements, polyesters for coil coatings have traditionally been prepared with neopentyl glycol. However, the superior flexibility and excellent weatherability of polyesters made from *MPDIOL* glycol has led several coil coating producers to convert to this new diol.

Until recently, the use of polyesters for can coatings was limited to beer and beverage (B&B) exterior basecoats in the US. However, recent concerns over the health effects of bisphenol-A are prompting suppliers to reevaluate the use of polyesters in interior can applications as well. *MPDIOL* glycol is FDA–approved in coatings for direct food contact under 175.300(b)(3)(ii) and (vii)(c) and is on the polymer exemption list (60 FR 16334). MPDiol is also fully registered under REACh, which has eliminated the previous need for polymer notification.

Polyester Resin Synthesis

Typical formulations blend water-reducible acrylic and polyester resins in melamine-crosslinked baking enamels. The following examples, however, demonstrate that all-polyester enamels can also meet the performance requirements for this application and may also be suitable for interior can and some coil coating applications.

Resin Component	Resin EB-17 Parts weight	Resin EB-18 Parts weight
MPDIOL glycol	217.9	217.9
TMP[1]	39.0	45.0
TMA[2]	20.3	20.3
Isophthalic acid	342.0	346.5
Fascat 4100	0.61	0.61
TMA[2]	29.4	29.4
Total	649.2	659.7

[1] Trimethylolpropane
[2] Trimellitic Anhydride

Procedure

1. Charge all the materials except the catalyst to a well-insulated reactor equipped with a thermometer, inert gas sparge, stirrer and overhead system (Heated PG partial condenser and a cold water condenser; PG bath maintained at 110°C to control the overhead temperature.).
2. Heat to 115°C; then add the esterification catalyst.
3. Increase the reactor temperature to 210°C while maintaining the overhead temperature around 95°C.
4. Maintain the reactor temperature until the acid number falls below 10 mg KOH/g.
5. Cool to 182°C and charge the remaining TMA. Maintain that temperature until the acid value reaches ~30 mg KOH/g.
6. Cool to 160°C and dilute to 70% solids with ethylene glycol n-butyl ether (EB) or a suitable non-HAP glycol ether. Solvent addition should be complete in 30 minutes.

Resin Properties

Property	Resin EB-17	Resin EB-18
Mn/Mw	4,400/8,900	4,300/8,600
Polydispersity	2.0	2.0
Acid Number, mg KOH/g	28	29
OH Number, mg KOH/g	80	85

Dispersion of Polyester Resins

Materials	Dispersion WB-17 Parts weight	Dispersion WB-18 Parts weight
Polyester Resin Solution	815.0	821.4
Dimethylethanolamine (DMEA)	16.2	16.2
Distilled water	810.0	810.0
Total	1641.2	1647.6

Procedure

1. Charge the resin solution into a mixing vessel equipped with an agitator.
2. Add the DMEA/distilled water mixture over at least 60 minutes with agitation.
3. Continue the agitation for another 5 minutes until the mixture is homogeneous.

Dispersion Properties

Properties	Dispersion WB-17	Dispersion WB-018
% Solids	30-35%	30-35%
Viscosity/cps Initial 5 weeks 10 weeks	 11,520 10,720 11,900	 8,800 8,560 8,800
pH	7.6	7.8-9.0
Appearance	Translucent clear	Translucent clear
Stability at 50°C, cps Initial 1 week 5 weeks 11 weeks	 6,480 11,520 10,720 11,900	 5,480 8,800 8,560 8,800

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Starting Formulations for Waterborne Can Coatings

Components	Coating CC-17 Parts weight	Coating CC-18 Parts weight
Dispersion	200.0	200.0
Titanium dioxide	100.0	100.0
Surfynyl® 485W	0.4	0.4
Cymel® 303	16.0	16.0
BYK® 301	1.6	1.6
Water	adjust to 76 ku	adjust to 76 ku

Blending Procedure

1. Weigh dispersion, add to a Dispermat-type mixer. Stir at constant speed.
2. Add 30% of the glass beads (based on the weight) of the mill-based formulation.
3. Increase the mixing speed until a vortex is created in the mill-base medium.
4. Add water occasionally to compensate for evaporation and balance the vortex.

Can Coating Properties

Properties	CC-17	CC-18
Brookfield Viscosity, cps Initial 5 weeks 10 weeks	510 4,560 3,520	510 8,800 11,000
VOC Content, lbs/gallon	1.82	1.82
% Solids	49.5	49.2
Dry Film Thickness/microns	10-12	10-12
0T Bend	Slight stain	Slight stain
Adhesion (untreated aluminum)	100/100	100/100
Bend Test - 2 mm	Pass	Pass
Boiling water test (90°C x 90 minutes) Adhesion Gloss retention	 100/100 99%	 100/100 98.5%
Scratch resistance	100 grams	100 grams
Konig Hardness	203	198
Impact Test (8 lb ft)	Pass	Pass
Initial 60° Gloss 11 weeks	84 85	84 87
Overbake resistance (190°C x 60 minutes) Gloss Retention Color change, ΔE	 97% 0.52	 96% 0.33

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Raw Materials	**Suppliers**
MPDIOL glycol	Lyondell Chemical
Fascat® 4100	Arkema Inc.
Surfynyl® 485W	Air Products
Cymel® 303	Cytec
BYK® 301	BYK Chemie

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