Application Data

MPDiol® Glycol

Weatherability of Melamine Cured MPDiol Glycol-Based Polyester Coatings

General Information

MPDiol does not undergo Nourish Type II degradation. In fact MPDiol exhibits weatherability performance of neopentyl glycol. This is contrary to what is expected of this type of polyol but the explanation can be easily arrived at by looking at frontier orbital theory and field results.

Key Features and Benefits

Liquid Glycol: MPDiol is supplied as a pure pumpable liquid and requires no additional solvents for processing. MPDiol's liquid state eliminates the need for solvent cook-off prior to the addition of diacid. Esterification rates for the same acid value are up to 30% faster with MPDiol.

Versatile Starter: The diprimary nature of MPDiol ensures better reactivity with diacids. MPDiol is liquid at 100% solids and is therefore pumpable as supplied. It can be used as the glycol of choice in a number of base resins in a number of applications, namely, high solids, coil, and polyurethanes.

Weatherable Polyesters: Polyesters resulting from the reaction of MPDiol with diacids such as adipic, isophthalic, phthalic and mixtures thereof are as weatherable as NPG based resins that are preferred for outdoor applications. This is a result of lack of electron density surrounding the LUMO of the MPDiol based ester preventing it from readily participating in a Beta-hydrogen abstraction. This makes the resulting polyester stable and weatherable.

Resins Preparation for Accelerated Weathering Testing

Several resins were synthesized under commonly practiced procedures for the synthesis of polyesters. Tests were performed using accepted ASTM methods. The coatings films were studied using several ASTM accelerated testing methods including QUV-B313, Xenon arc, QUV-A340, and Emmaqua® NTW. Polyester resin preparations included recipes for coil and high solids polyesters.

Three coil coatings were produced and formulated using neopentyl glycol, MPDiol, and propylene glycol as the diol in the polyester resin. (See Table 1) Coil coatings formulated with the resins outlined in Table 2, NPG and MPDiol weathered similarly in all tests. In the Emmaqua test, Control PG showed to be distinguishably the best. Best performers under all testing methods, however, were the only ones selected for outdoor exposure testing. Control NPG and Coil-B, were selected for Florida exposure testing. The outdoor test confirmed the accelerated weather testing results. After 21 months of exposure it was determined that in this coil formulation, the MPDiol based resin at higher isophthalate content, weathers equally to the NPG based control resin. (See Figure 1) This is unexpected and can be explained by looking at molecular mechanics models for the exposed orbital. (See Molecular Mechanics Section)

Application Data

MPDiol® Glycol

Weatherability of Melamine Cured MPDiol Glycol-Based Polyester Coatings

Resin Components	*Control NPG*	*Coil-A*	*Control PG Weight*	*Coil-B*
Diol	411.4	376.8	349.9	366.7
Isophthalic Acid	308.3	325.9	340.5	544.2
Adipic Acid	153.7	162.5	169.8	79.1
Phthalic Anhydride	126.6	133.8	139.8	-
Properties				
Acid Number mg KOH/g	6.7	6.8	5.0	6.5
Hydroxyl Number mg KOH/g	26	28	40	23
Molecular weight (avg. num.)	2200	2300	1370	3200
% Solids	65	65	65	62
Viscosity (Gardner-Holdt)	Z	Y/Z	V/W	Z4
Glass Transition	7	-5	5	13

Table 1. Composition and properties of polyester resins, based on MPDiol test resins versus neopentyl glycol controls, used for coil coatings application.

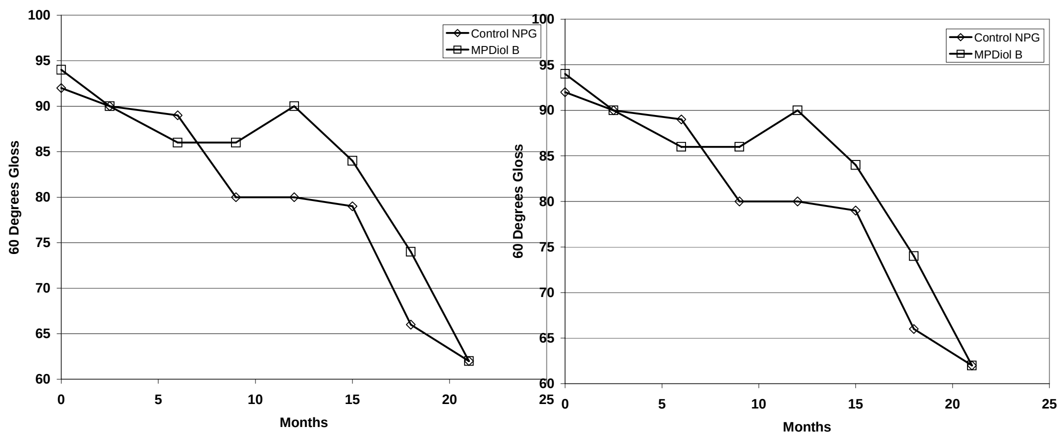

Figure 1. Florida Exposure results for coil coatings based on MPDiol and neopentyl glycol. (Kronos 2090 Titanium dioxide)

The second group of resins was studied for High-solids polyester formulations. In this study the amount of adipic and phthalic acids were varied to achieve different performance in the MPDiol based resins and then compared to a neopentyl-based polyester. (See Table 2) The films were studied in the same manner as the coil coatings. The results for this group of resins showed that for QUV-B313 the NPG Control outperformed the MPDiol based resins. This was; however, not confirmed by the other accelerated weathering tests where all the resins seemed to behave either similarly or the MPDiol resins were slightly better than the NPG. This discrepancy is not unusual. In the Florida exposure test, the resins appear to behave more like the QUV-A, Xenon, and Emmaqua tests where higher isophthalate content helped the weatherability of the resin. (See Figure 2) This is not expected and is somewhat puzzling unless the aromatic ring is acting as though an electron sink making the surface more available to scavenge electrons.

Application Data

MPDiol® Glycol

Weatherability of Melamine Cured MPDiol Glycol-Based Polyester Coatings

Diol Component	*Control NPG* Mole Ratio	*HS-A*	*HS-B*	*HS-C*	*HS-D*
Neopentyl glycol	6.12				
MPDiol		6.12	6.12	6.12	6.12
Isophthalic acid	2.19	2.19	3.28	3.85	4.38
Adipic acid	2.19	2.19	1.10	0.53	
Trimethylol propane	0.587	0.587	0.587	0.587	0.587
Properties					
Acid Number (mg KOH/g)	3.3	5.2	1.1	2.1	1.1
Hydroxyl Number (mg KOH/g)	246	260	247	248	240
Molecular weight (avg. num.)	833	730	792	759	792
% Solids	79.2	79.5	80.1	80.4	81.1
Viscosity (Gardner-Holdt)	Y/Z	V/W	Z1	Z4	Z6/Z7

Table 2. Composition and properties for polyester resins, based on MPDiol test resins and neopentyl glycol controls, used in high solids applications.

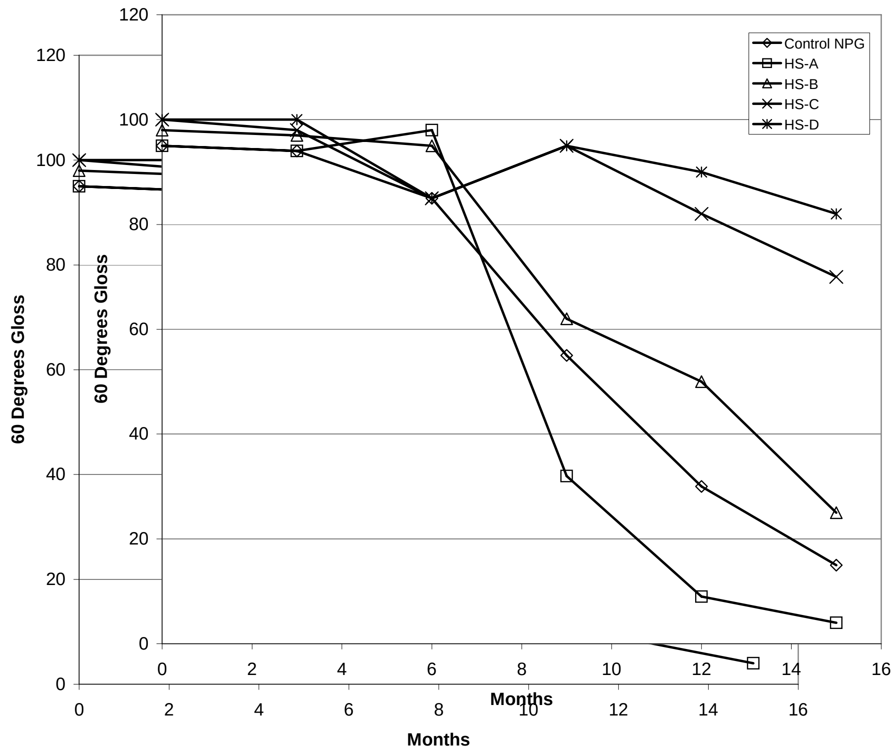

Figure 2. Florida exposure results for MPDiol and neopentyl glycol based high-solids coatings.

Control outperformed the MPDiol based resins. This was; however, not confirmed by the other accelerated weathering tests where all the resins seemed to behave either similarly or the MPDiol resins were slightly better than the NPG. This discrepancy is not unusual. In the Florida exposure test, the resins appear to behave more like the QUV-A, Xenon, and Emmaqua tests where higher isophthalate content helped the weatherability of the resin. (See Figure 2) This is not expected and is somewhat puzzling unless the aromatic ring is acting as though an electron sink making the surface more available to scavenge electrons.

Molecular Mechanics

The general consensus for polyester weatherability is the stability of the hydrogen exposed to radical abstraction. Generally, the beta hydrogen is believed to be susceptible to abstraction therefore all polyesters having one, are deemed unusable in highly exposed outdoor applications. There is, however, a more scientific way of determining reactivity of a molecule rather than relying on a rule of thumb. One of the simplest ways of comparing sites for radical reactivity is the frontier molecular orbital (FMO) method. The highest occupied molecular orbital (HOMO) and lowest unoccupied orbital of the molecule (LUMO) determine how reactive the molecule will be under reaction conditions in this case free radical oxidation. When NPG and MPDiol diacetate models are analyzed using this model the results indicate that the two polyesters are predicted to react at the alpha hydrogen. (See Table 3) Alpha hydrogen is common to all polyesters so the difference in reactivity between various resins having different glycol and acid backbones should be attributed to the electron density surrounding this hydrogen and not the adjacent beta hydrogen. This would clearly explain why the MPDiol based polyesters showed similar weatherability to the NPG based resins. The density around the MPDiol based polyester linkage shows little to no electron density at the beta hydrogen site. The same acetate has alpha hydrogen where most of the electron density is concentrated and therefore one would predict that this is where degradation will occur as this hydrogen reacts with a radical. Similarly, for NPG, the alpha hydrogen is electron density rich indicating it too will degrade at this point in the molecule. Considering that NPG has no beta hydrogen this is the only likely site for degradation. Additionally, the results predict that both NPG and MPDiol will tend to react in the same manner. Qualitatively, considering the steric environment of each glycol one would also predict that the rate of degradation should be similar. The Florida Exposure testing supports both arguments; the FMO and our qualitative assessment of the spatial interactions for MPDiol's unexpected weatherability. The differences experienced in some of the accelerated weathering tests can be attributed to experimental variability.

Atom	*Group*	*NPG*	*MPDiol*
H	CH_3 (Diol)	0.004	0.004
H (beta)	CH		0.017
H (alpha)	CH_2	0.051	0.050
H	Acetate	0.002	0.003

Table 3. Frontier Density of MPDiol and NPG diacetates

Application Data

MPDiol® Glycol

Weatherability of Melamine Cured MPDiol Glycol-Based Polyester Coatings

Summary

Given the discrepancies between theory and accepted accelerated weathering of coatings we sought to understand and confirm using real time testing of MPDiol based polyester coatings. The FMOC theoretical model best supported the results where the polyester is degraded by oxidation by a free radical chain propagation mechanism. The model clearly indicates that the alpha hydrogen is responsible for the reactivity of the polyester towards this free radical reaction. This was confirmed when the various polyesters were subjected to Florida weathering and showed minimal differences in weatherability. Any differences they may occur will be mostly due to hydrophobicity, glass transition temperatures and other final film properties that may affect the coatings ability to withstand the environmental conditions.

World Headquarters
Lyondell Chemical Company
1221 McKinney
Houston, TX 77010
Tel (713) 652-7200
Toll-free (888) 777-0232
MSDS Hotline: (800) 700-0946

European Headquarters
Lyondell Chemical Europe, Inc.
P. O. Box 2416
3000 CK Rotterdam
The Netherlands
Tel (31) 10 275-5500
Tel (33) 3 44 24 92 05 (tech svc)

Lyondell South America
Av Roque Petroni Jr,
999, cj 123
Sao Paulo, SP 04707-910
Brazil
Tel (55) 11-5185-9300

Asian Headquarters
Lyondell Asia Pacific, Ltd.
41st Floor – The Lee Gardens
33 Hysan Avenue
Causeway Bay, Hong Kong
Tel (852) 28822-668
Tel (33) 3 44 24 92 05 (tech svc)

2413-V3-0304
Supersedes 2413-V2-0303