**POLYESTER Resins**

**Bang for The Buck**

New polyester resins for durable coatings allow formulators to obtain high performance without breaking the bank.

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This article describes the preparation and use of high-performance, yet inexpensive, polyesters for durable coatings. Starting formulations based on these polyesters and coating properties are also compared to commercial high-performance systems.

MPDiol Glycol (2-methyl-1,3-propanediol) is a relatively new performance diol with a unique combination of properties. Its branched structure imparts flexibility in polyesters and lowers their viscosity. These features make MPDiol particularly useful for the production of polyesters for can, coil, high-solids, gel coats and powder where a combination of flexibility, toughness and weatherability are required. It also allows greater use of terephthalic acid and phthalic anhydride, two inexpensive raw materials.

After acrylics, polyesters are the most common type of resin used in high-performance coatings. This is due to their low cost, good exterior durability, excellent mechanical properties and versatility. In 1997, the estimated annual U.S. demand was more than 900 MM pounds (1).

Alkyd resins, or oil-modified polyesters, are the largest type of
polyester and have been declining at a rate of 2 to 3 percent per year mainly because of VOC regulations. Other polyesters, on the other hand, have been growing at an average annual growth rate of 6 percent, spurred by the growth of powder and extrusion coatings, and unsaturated polyesters for gel coats. Lately, saturated polyesters for coil coatings have also experienced strong growth in the United States due to strong cyclical demand for construction materials.

Aside from VOC restrictions, several new regulations, raw materials and health concerns are driving growth or reformulations in the polyester resin market. In the composites area, resin producers are looking for lower-viscosity resins to reduce their styrene emissions and are reevaluating UV-curable systems. Recent concerns over the long-term health effects of bisphenol-A-based epoxies are also prompting can-coating manufacturers to evaluate polyesters for the interior of can coatings.

New raw materials, such as 2-methyl-1,3-propanediol (MPDiol), are also generating new opportunities to develop high performance polyesters at a lower cost. This article describes several types of preparations, formulations and performances of polyesters for coil, exterior can, high solids and gel coats.

POLYESTER SYNTHESIS

Polyesters are prepared by condensation of diacids or anhydrides and diols. The byproduct water must be removed from the reactor by distillation. This makes polyester synthesis more energy intensive than, say, acrylate polymerization, which produces no water and is exothermic. Condensation of diols with anhydrides produces less water and is, therefore, preferable over condensation with diacids. However, the choice of inexpensive anhydrides is limited to phthalic and maleic anhydrides.

Several other factors affect the cost of polyesters, such as raw material costs, polymerization kinetics, energy requirements and batch yields. Proper selection of raw materials is the most important factor 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.

Diols with primary hydroxyl groups and high boiling points, such as MPDiol and 1,6-hexanediol, react faster than those with secondary hydroxyl groups or low boiling points. The melting point of the diol affects both its handling and the rate of reaction, especially with relatively insoluble diacids such as terephthalic acid. Liquid diols can be pumped into the reactor and help solvate solid acids and anhydrides. This generally results in faster esterification kinetics and lower production costs.

RAW MATERIAL SELECTION

Typical U.S. prices for polyester raw materials are on page 36.

Maleic anhydride is unsaturated and is used predominantly in the synthesis of unsaturated polyesters for gel coats and composites. Phthalic anhydride is mostly used in lower-performance coatings because it is perceived to produce polyesters less resistant to UV light and water than the more expensive isophthalic or adipic acids. Terephthalic acid is used extensively in powder coatings because of its low cost and hardness. Its lower UV stability and esterification rate limits its use in other coating systems.

Higher-priced diols such as neopentyl glycol are still predominantly used for weatherable polyesters. Some neopentyl glycol producers have also advanced the theory that polyesters degrade by free-radical abstraction of the diol beta-hydrogens, followed by carbon-carbon bond cleavage.

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weatherable coatings suitable for exterior applications, despite the fact that MPDIol has a beta-hydrogen. Frontier molecular orbital calculations also predict that other sites on the polyester are far more susceptible to free-radical attack (3). More recently, we have found that a similar polyester is suitable for exterior can applications and that low-cost MPDIol/anhydride polyesters can produce weatherable high-solids coatings and gel coats. This information is reviewed below.

**COIL COATINGS**

Performance requirements for coil and other types of coatings apply to both the formulation and film properties. Formulations must be storage stable, have low-VOC contents and be inexpensive. Coil coatings are applied to flat metal stock, heat cured and the coated metal is then formed into various shapes. Typical applications include aluminum siding, gutters, truck trailers and appliances. Because the parts are coated before they are formed, flexibility and adhesion are critical performance requirements for coil coatings. Typical requirements include zero T-bend flexibility; excellent adhesion, hardness and abrasion resistance, excellent exterior weatherability, stain, detergent and corrosion resistance.

Because of the extreme weatherability requirements, polyesters for coil coating applications had traditionally been prepared with neopentyl glycol. However, the superior flexibility and excellent weatherability of polyesters made from MPDIol (2-methyl-1,3-propanediol) has led several coil coating producers to convert to this new diol. A representative resin composition, coating formulation, and performance data are listed in this article. (This polyester coating outlasted a commercial neopentyl glycol-based coating under Florida exposure conditions.)

**CAN COATINGS**

The use of polyesters for can coatings is limited to beer and beverage (B&B) exterior basecoats. However, recent concerns over the health effects of bisphenol-A are prompting suppliers to re-evaluate their use in interior applications as well. The use of polyesters in exterior basecoats is interesting in that it demonstrates the utility of polyesters in low-VOC waterborne formulations for a fairly demanding coating application.

Typical formulations blend water-reducible acrylic and polyester resins in a melamine-crosslinked baking enamel. The following example, however, demonstrates that an all-polyester enamel can also meet the performance requirements for this application and may also be suitable for interior applications.

The performance data mentioned in this article demonstrates that an all-polyester enamel can meet the demanding performance requirements for B&B and even food cans. Boiling water resistance is required in beer and beverage cans because of the pasteurization step that follows the coating and filling operation.

Food cans are subjected to even higher heat conditions for sterilization and must retain gloss and low color under retort conditions. This suggests that properly formulated polyester enamels may be suitable for interior can applications as alternatives to bisphenol-A-based epoxy-acrylates.

**HIGH-SOLIDS COATINGS**

High-solids, thermosetting, solventborne polyester coatings are used in a variety of applications, including primers for automobiles and topcoats for metal furniture and appliances. Low-viscosity polyesters are obtained by maintaining a 15 to 20 percent excess of diol over diacid. This limits the polyester molecular weight (Mn) to less than 2,000, which lowers the viscosity but also typically reduces the coating’s weatherability. Popular diols are neopentyl glycol and 2,2,4-trimethyl-1,3-pentanediol. Small amounts of multifunctional polyols, such as trimethyl-
lolpropane, are also used to increase the crosslink density and improve film properties. On the acid side, phthalic anhydride is often used to lower cost and adipic acid is used to improve flexibility and UV-resistance. A typical resin composition is 45 percent neopentyl glycol, 40 percent phthalic anhydride and 15 percent adipic acid (4).

Using MPDiol instead of neopentyl glycol increases polymerization rates and improves the flexibility of the polyester, requiring less adipic acid to be used. This lowers raw material and production costs, gives formulations superior storage stability and provides coatings with good mechanical properties and excellent weatherability. This is illustrated by the following example.

The film properties of this low-cost, high-solids coating were comparable to those of a commercial control, except for lower impact resistance and higher hardness (100/80 and 2H for control). These properties can be easily adjusted by lowering the melamine/polyester ratio to 20/80 or increasing the adipic acid content. On the other hand, the Florida weatherability of the low-cost polyester was significantly better than the commercial control.

**GEL COATS**

Consumption of unsaturated polyesters for gel coats in the United States was estimated to be over 60 MM pounds in 1996 (5). Gel coats are the exterior coatings for fiberglass-reinforced composite products such as recreational boat hulls, bath tubs and shower stalls and exterior truck parts. They are considered solventless systems because styrene is used to dissolve the resin and becomes part of the coating during the curing process. However, gel coats and composites fabrication emits significant amounts of styrene, which has recently become an issue in the U.S. As a result, gel coat manufacturers are looking for lower-viscosity polyesters to reduce the styrene content of their coatings.

Proper selection of raw materials is critical in this application as well. Cost and performance requirements vary significantly in this market, but gel coats are considered to be high-end products and have stringent performance requirements. In addition to maleic anhydride, the standard raw materials for gel coat polyesters have been neopentyl glycol and isophthalic acid. This is because the resulting gel coats have superior mechanical, UV and corrosion resistance compared to resins made from propylene glycol and phthalic anhydride (“ortho” resins). However, our research shows that properly designed, MPDiol-based ortho resins can match the performance of neopentyl glycol-based “ISO” resins and provide the polyester manufacturer with significant cost-saving opportunities. Based on typical raw material costs in the United States, the MPD/PAN resin mentioned earlier is estimated to cost 20 cents per pound less than an NPG/ISO resin. This is very significant, considering their performance is comparable.

Aside from lower cost, the MPD ortho resin had lower solution viscosity, improved storage stability and yellowed less under UV-A exposure. The mechanical properties of clear castings and gloss retention under UV-A exposure were comparable to the neopentyl glycol/iso resin.

**CONCLUSION**

A number of factors are creating opportunities to develop new high-performance polyesters at lower cost. Strong growth in powder coatings, composites and coil are increasing the market need for polyesters. Health concerns over bisphenol-A are also opening the door for the use of polyesters in traditional epoxy applications, such as interior can coatings.

Finally, new raw materials, such as MPDiol, are allowing for greater use of inexpensive diacids, such as phthalic anhydride and terephthalic acid, for the manufacture of high-performance, yet lower-cost, polyesters.

**REFERENCES**


For more information, please call Lyondell at 1-888-777-0232.

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