Manufacturing Efficiencies Further Enabled by Recent Developments in Methylidene Malonate Chemistry

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Recent work at Sirrus has focused on the development of multifunctional methylene malonates through transesterification of ester side groups with numerous diols. These can give rise to difunctional methylene malonates that permit crosslinking, and multifunctional polyester-type macromers with high molecular weight (>700 Dalton). These products can be used as raw materials for a variety of coating applications, thanks to their film forming capabilities and the high-count alkene functionality distributed across the main chain, which tends to crosslink when exposed to basic or nucleophilic constituents in primer/sealers or basecoats.

Using 100 percent-reactive methylene malonate monomers, difunctionals, multifunctionals and prepolymers, manufacturers of paints, coatings and other products can dial in a wide range of properties to produce a variety of high-performing polymer products that cure rapidly at low or ambient temperatures.

Performance testing has demonstrated the versatility and power of this platform in coating applications. Applying this new technology, clear coatings have been made to perform as well as a benchmark urethane isocyanate often used in refinishing, only with safer, less costly and more energy-efficient processing characteristics.

**POTENTIAL FORMULATION OPTIONS**

1. **Reactive Coatings with Crosslinking**

Perhaps the most direct applications of methyldiene malonates in coating formulations may involve liquid reactive coatings based on the monomers themselves—methyldiene malonate monomers that can readily polymerize anionically or free radically to produce coating films. Formulations may be based on a broad range of methyldiene malonate esters, potentially offering a wide range of functional groups (as found with acrylate esters). Formulation options may include two-component ambient cured coatings (employing, for example, amine initiators), one-component thermally cured coatings employing free radical or anionic initiators, or UV-cured coatings incorporating photoinitiators. Crosslinking may be effected using multi-functional methyldiene malonate monomers. These may include dimers, trimers or other multifunctional adducts; methyldiene malonate capped prepolymers; adducts of methyldiene malonate with isocyanates; or a broad range of other polyfunctional adducts.
2. Crosslinking via Michael Addition

Additionally, multifunctional methyldiene malonates may potentially be employed to crosslink more conventional polymers, oligomers or polyols such as acrylic polyols. For example, isocyanates are commonly used as crosslinking agents in two-component coating formulations that cure at ambient temperatures. Since methyldiene malonates can undergo triggered crosslinking reactions via Michael addition to amine or hydroxyl groups as well as amine triggered polymerization, it may be possible to design two-component methyldiene malonate crosslinked coating systems that cure at room temperature. For example, monomers with multiple methyldiene groups (dimers, trimers, tetramers, etc.) may be useful as crosslinking agents for hydroxyl, amine or carbamate containing acrylic polyols. Additionally, amine containing primers based on epoxy chemistry may initiate or accelerate the crosslinking or polymerization reaction for substrate-activated coatings. Compatibility with pigments or other additives may represent a formulation challenge. Potential methyldiene malonate based crosslinkers may include dimers, trimers or other multifunctional esters, methyldiene malonate capped prepolymers, and adducts with isocyanates, as well a broad range of other polyfunctional adducts similar to those found with multifunctional acrylates.
**FORMULATION BENEFITS**

Clear coatings made using Sirrus technology lower cure temperatures and solvent content relative to incumbent automotive OEM clear coatings while demonstrating high gloss, UV stability, and environmental resistance in preliminary testing. We believe these benefits may be transferable to a broad range of industries where reduced temperatures and lower VOCs will enable higher product quality, implementation of novel design features and improved manufacturing efficiency.

![Diagram showing lower cure temperature and solvent content](image)

For more information regarding our unique monomer technology and performance data, please contact [Jeff Sullivan at jeffsullivan@sirruschemistry.com](mailto:jeffsullivan@sirruschemistry.com) or [Andy Palsule at aniruddhapalsule@sirruschemistry.com](mailto:aniruddhapalsule@sirruschemistry.com).