# Formulating with Millathane® Millable Polyurethanes

Millable polyurethanes are generally compounded similar to other types of rubber, but there are some factors to consider and some ingredient interactions to be aware of. This bulletin is meant to be a guideline for ingredient selection for Millathane® millable polyurethanes.

## MILLATHANE GRADE CHOICE

In deciding which grade to use, the first question is whether polyether or polyester polyurethanes are preferable. Polyether types are inherently better for water and hydrolysis resistance than polyester types and would generally be used for applications requiring long term water or humid environment exposure. Polyester grades, however, can be very good for moderate exposures to these conditions, with the addition of hydrolysis stabilizers like Millstab™ P.

Polyester types are better for oil, solvent, heat and compression set resistance than polyether grades, with Millathane® 66 being best for heat and set resistance, and Millathane® 5004 being best for oil and solvent resistance. Because all polyester polyurethanes are prone to the effects of hydrolysis, it's highly recommended that Premilled grades, which contain 1.5 phr of Millstab P, be used. Additional amounts of Millstab P can be added for improved protection.

Note that different grades of Millathane® can often be blended together, to modify processing characteristics or cured properties. Examples are Millathane® E34/76 blends and Millathane® 5004/66 blends.

## CURE SYSTEMS

All Millathane® grades can be peroxide cured, and some grades can be sulfur cured. Generally, peroxide cures will give better heat and compression set resistance compared to sulfur cures, but sulfur cures will generally give higher strength (tensile and tear) properties along with better abrasion resistance. Sulfur cures are more prone to reversion upon over-curing or high temperature curing, while peroxide cures are much more resistant to reversion.

## PEROXIDE CURES

The peroxides commonly used with other rubber types will generally work well in millable polyurethanes, including DBPH and dicumyl peroxide. It's important to note that different levels of peroxides are needed for different grades. The following is a guideline to the peroxide levels that generally give the best balance of properties with different Millathane® grades.

| Typical levels of DCP-40 or DBPH-50 | |
|---|---|
| Millathane® HT | 0.5 - 1.2 |
| Millathane® 97 | 1.2 - 2.5 |
| Millathane® CM, E34, 55, E40, 76 | 2 - 3 |
| Millathane® 26 | 4 - 5 |
| Millathane® 5004, 66 | 4 - 8 |

Coagents are commonly used in peroxide cures to modify properties. TAC or TAIC can be used at low levels (0.5-2 phr) to improve set properties, although tear strength and abrasion resistance may be diminished somewhat. Liquid methacrylates like TMPTMA (SR-350) and DEGDMA (SR -231) are commonly used, sometimes at high levels, to increase hardness and improve processing. Blends of trifunctional methacrylates (e.g., SR-350) with difunctional methacrylates (e.g., SR-231 or SR-297) give better properties in high hardness compounds than using trifunctional methacrylates alone. Liquid polybutadienes (e.g., Ricon 154, Lithene AH) can be uses to plasticize and improve compression set, although these are not as effective as the methacrylates.


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### SULFUR CURES

The original combination of MBTS, MBT, Thanecure® ZM and sulfur, developed by DuPont in the late 1950's for Adiprene C (now, Millathane® CM), is still be best cure system for sulfur curable millable polyurethanes. The typical levels of these curatives now used are 4/2/1/1.5 (MBTS/MBT/Thanecure ZM/Sulfur), which gives a good combination of cure speed and physical properties. The curative levels used in most of the original DuPont work, 4/1/0.35/0.75 (sometimes referred to as the "classic" cure system) give good properties with better heat resistance than the standard curative levels, but curing needs to be done for long times (30-60 minutes) at low temperatures (140°-150°C) to get good cures. Curing compounds using the "classic" cure system at higher temperatures usually results in pock-marking in the cured samples. Zinc stearate, which functions as an activator and process aid, is also used in sulfur cure systems at 0.5 phr.

### ISOCYANATE CURES

The isocyanate cure system, a combination of Thanecure® T9SF, HQEE (finely ground), and accelerator (e.g., Bismate), can be used with several Millathane grades to achieve high hardness compounds, up to 65 Shore D, with exceptional tensile and tear strength properties and very good abrasion resistance. Millathane® 26 gives the best properties with this cure system, giving tensile strengths up to 7500 psi (52 MPa) and Tear C values up to 800 lb/in (140 kN/m). Millathane® 97, Millathane® 76, Millathane® E34 and Millathane® 55 can also be cured with this cure system, with somewhat lower, but very good, strength properties.

Important things to note in using this cure system:

- compounds have very short shelf life. At RT, compound must be used within 24 hours. Freezer storage, at -10°C, can give 2 – 4 (or more) weeks shelf life.
- compounds need to be mill mixed, and cured at low temperatures (120°-135°C)
- small amounts of TDI may be generated during mixing and curing, so ventilation and PPE may be required (refer to the MSDS/SDS for Thanecure T9SF).

### ANTIOXIDANTS

Heat resistance of peroxide cured polyether grades (e.g., Millathane® CM, E34, E40, 55, 97*, 26) will generally be improved by the addition of antioxidants. Several that have been found effective are Irganox (or Songnox) 1010, Irganox 1076 and Naugard 445. The combination of Irganox 1010 and Naugard 445, at 0.5-1.0 phr each, will be sufficient for most applications. Antioxidants give minimal benefit to polyester Millathane grades (which are inherently better for heat resistance than polyether grades) and to sulfur cured compounds.

- A minimum of 0.25 phr antioxidant is required in all Millathane 97 compounds.

### FILLERS

For black compounds, any of the rubber carbon blacks can be used. N330 is very commonly used, as it gives a good combination of excellent properties and easy mixing. For non-black compounds, precipitated silicas (e.g., HiSil 233 or Ultrasil VN3) are very commonly used and give excellent properties. Fumed silica gives somewhat higher hardness and reinforcement than precipitated silicas, and is used for transparent compounds (of Millathane® 97). Silane coupling agents (e.g., Silquest A189 for sulfur cures, Silquest RC-1 for peroxide cures) are often used with silicas to improve properties, primarily tear strength and abrasion resistance.


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### PLASTICIZERS

Many of the plasticizers that are used in polar rubbers like NBR can also be used in Millathane® compounds. TP-95 (DBEEA) is very commonly used because it is very compatible with millable polyurethanes and gives good properties and processing. Other commonly used plasticizers are Mediaplast NB4 and coumarone indene resins (e.g., Cumar P10), although the latter cannot be used in peroxide cures because they will retard curing.

### PROCESS AIDS

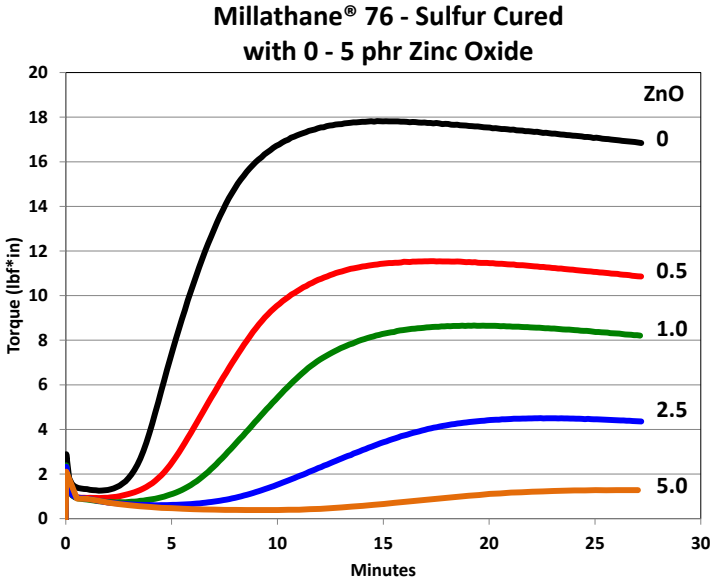
Most compounds contain small amounts of process aids to prevent mill/mixer sticking. Sulfur cures will always have 0.5 phr of zinc stearate and peroxide cures will typically have about 0.25 phr stearic acid. Additionally, a small amount (0.5-2 phr) of process aids like Struktol WB222, Dispergator FL, and/or low melt polyethylene (AC617A) are often used.

### INGREDIENTS TO AVOID

**Zinc oxide** — This ingredient will retard cures of millable polyurethanes, especially polyester grades like Millathane® 76, where even 0.5 phr affects the curing significantly and 5 phr gives virtually no cure activity. The effect is not as severe in polyether grades like Millathane® E34, especially at low levels.

**Calcium oxide** will also retard curing of millable polyurethanes, and should not be used in Millathane® compounds (see chart below).

**Sulphenamide accelerators** — These do not function well in polyurethane cure systems.

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