



Millathane® 76 and Millathane 76M (Premilled)

Millathane 76 is a sulfur or peroxide curable polyester millable polyurethane rubber, used in many applications because of its excellent oil resistance, high damping characteristics and high strength and abrasion resistance properties.

Millathane 76 is available in two forms: Virgin bales and Premilled sheets. Millathane 76 Premilled contains 1.5 phr of Millstab™ P, a polymeric carbodiimide hydrolysis stabilizer. It is often recommended that Millathane 76 Premilled be used, as the incorporated hydrolysis stabilizer provides protection to the polymer, to mixed compounds and to the finished product.

Product Description

Chemical Composition:	Synthetic rubber based on ester/TDI polyurethane
Specific Gravity:	Approximately 1.22
Storage stability:	2 years from date of manufacture (stored under dry and cool conditions)

Part Number	Mooney Viscosity ML(1+4)/100° C	Appearance	Package size/carton
M-0076-35 (Virgin)	25 – 45	Amber to light solid bales	45 pounds (20.4 kg)
M-0076-45 (Virgin)	35 – 55		
M-0076-55 (Virgin)	45 – 65		
M-0076-65 (Virgin)	55 – 75		
M-0076M-40 (Premilled*)	35 – 45	Amber to light solid sheets	50 pounds (22.7 kg)
M-0076M-50 (Premilled*)	45 – 55		

*Premilled - Contains 1.5 phr of carbodiimide hydrolysis stabilizer (Millstab™ P)

Processing

Millathane 76 is processed by techniques which are common to the rubber industry. Compounds can be mixed on open mills or in internal mixers. Very often a compound can be mixed in one step including the vulcanization chemicals. Molded articles can be produced via compression, transfer or injection molding. Injection molding Millathane 76, mostly done with peroxide cures, provides very short cycle times, excellent flow and demolding and shows negligible mold fouling. Most compounds can be calendered for fabrication of rubber covered rollers or conveyor belting, or calendered sheets can be press cured or rotocured.

See the publication TIPS V2-1 for additional information on mixing and processing.

Properties

Vulcanizates based on Millathane 76 can be produced in hardnesses ranging from approximately 30 to 95 Shore A, and offer very good abrasion resistance, excellent oil resistance, good resistance to gas permeability and low resilience (high damping). Sulfur cured Millathane 76 compounds get *excellent* strength properties at low hardnesses (30-50 Shore A). Peroxide cures give improved compression set and heat aging properties.

Applications

The excellent balance of properties of Millathane 76 makes it a perfect choice for various rubber parts including seals, diaphragms, bushings, test pads, suction cups, rubber-covered rollers and solid tires.



Compounding

Reinforcing Fillers

Reinforcing fillers like N330 carbon black or precipitated silica increase the mechanical strength of Millathane 76 compounds. Fumed silicas such as Wacker HDK N20 or Cabosil M-5 will give somewhat higher reinforcement than precipitated silicas and will give translucent cured compounds (depending on other ingredients). Clay, talc and calcium carbonate can also be used as fillers to modify properties and processing, but are less reinforcing than silicas and blacks. Silane coupling agents like Silquest A189 and Si69 (in sulfur cures) and Silquest Y-15866, RC-1, or A172 (in peroxide cures) will improve the tear strength and set properties of mineral filled/reinforced compound and are recommended to be added at about 2% of the mineral filler content.

Plasticizers

TP-95 (DBEEA) is a plasticizer that is very compatible with Millathane76, with compounds containing 25 phr and more usually not showing signs of bleeding or incompatibility. Other plasticizers such as Medioplast NB-5 and Benzoflex 9-88SG can also be used to plasticize and soften compounds. Coumarone indene resins such as Cumar P10 and Cumar P25 can be used to plasticize sulfur-cured compounds and improve uncured tack, although high levels (>20 phr) may give tacky cured surfaces. The antistatic plasticizer Struktol AW-1 can be used to a limited extent, to lower surface resistivity, but may tend to bleed at levels over 10 parts. Vulcanized vegetable oils (factices) are often used in soft compounds to assist with plasticizer incorporation. Sulfur-free factice like Akrofax 758 is good for sulfur or peroxide cures; sulfur-containing factices can be used in sulfur cures only. White factices should not be used, as they retard the cure.

See the publication TIPS V4-4 for additional information on plasticizers.

Stabilizers/Antidegradants

Millathane 76, being a polyester polyurethane, is prone to the effect of hydrolysis, where water can attack the polyester linkage of the polymer chain. The effect is accelerated by higher temperatures or acidic conditions. The inclusion of a small amount (1-3 phr) of hydrolysis stabilizer such as Millstab™ P will greatly inhibit the effect of hydrolysis. Higher levels of stabilizer will generally provide improved or longer protection. Using *Premilled* Millathane 76, which contains 1.5 phr of Millstab P, is highly recommended and is a convenient way to include that amount of stabilizer in the compound, and the incorporated stabilizer improves shelf stability of the polymer as well.

Small amounts (0.5-2 phr) of antioxidants like Naugard 445 and Irganox 1010 may provide some benefit to the heat aging characteristics of Millathane 76 compounds.

Process Aids

Small amounts of process aids are normally used to prevent sticking to processing equipment and to improve flow during molding. For sulfur-cured compounds, the 0.5 phr of zinc stearate used as an activator is usually adequate. For more release, 0.5-2 phr of another process aid such as Struktol WB222 or Vanfre AP-2 can be used. For peroxide cures, 0.2-0.5 phr of stearic acid is used in place of zinc stearate. A low molecular weight polyethylene like AC617A, added at 1-4 phr, gives good release for calendaring and molding. Process aids are best added at the very beginning of the mix cycle, to prevent sticking to mills and mixing equipment.

Curing Agents: Sulfur and Peroxide Cures

The best physical properties and abrasion resistance are achieved with sulfur cures, while the best compression set, heat aging and reversion resistance comes from peroxide cures. The sulfur cure system is a combination of MBTS (4 phr), MBT (2 phr), Thanecure® ZM (1 phr) and sulfur



(1.5-2.0 phr), along with zinc stearate (0.5 phr), used as an activator. Sulfur dispersions, typically with about 20% process oil, are often used for optimal sulfur dispersion.

Peroxide cures can be used for better set and heat aging characteristics. Typical peroxides used are dicumyl peroxide and DBPH, typically used at about 0.6 – 1.2 phr active peroxide (1.5 – 3.0 phr of 40% active). The use of low levels of coagents such as triallyl cyanurate (TAC) and trifunctional methacrylates like SR350 (TMTDMA) increase the crosslink density and improve compression set. Blends of the difunctional methacrylates SR231 (DEGDMA) or SR297 (BGDMA) with the trifunctional methacrylate SR350 are recommended for high hardness compounds, as the blend gives a good balance of strength properties, elongation and set. High crosslink densities, seen with high peroxide and/or coagent levels, will improve compression set but strength properties and elongation may be adversely affected.

Vulcanization Conditions

Sulfur-cured compounds are typically molded at temperatures of 150° - 165°C; higher temperatures can give poor cures due to reversion. Peroxide-cured compound can be cured from 145°-175°C, depending on the peroxide, dimensions of the part etc. Rubber covered rollers can be vulcanized in hot air (electric) or steam autoclaves, but it is extremely critical to completely protect the compound from direct contact with steam and to not over-cure the rollers. Autoclave temperatures can range from 130°-150°C, with times dependent on roller size. *Please contact TSE for recommendations regarding roller compounding, fabrication and curing!* Millathane 76 cannot be cured in direct contact with open steam or hot air, and, hence, for applications like hose, its use is usually limited to inner liners. Calendered sheets can be press-cured, Rotocured, or cured in autoclaves (calendered into fabric liners, and then protected against steam contact).

Formulation Examples

71 Shore A Black Molding Compound

	XP-6616-E	Press Cured Properties, Cured 6 min/160°C	
Millathane® 76	100.0	Hardness Shore A	71
Zinc Stearate	0.5	TSE-100*, psi (MPa)	440 (3.0)
Millstab™ P	2.0	TSE-300*, psi (MPa)	1730 (11.9)
N 330 black	25.0	Tensile strength, psi (MPa)	4670 (32.2)
DBEEA (TP-95)	2.0	Elongation, %	565
Struktol WB-222	1.0	Tear Die C, lb/in (kN/m)	264 (46.2)
MBTS	4.0	Tear Die B, lb/in (kN/m)	506 (88.6)
MBT	2.0	DIN Abrasion, mm ³ loss	109
Thanecure® ZM	1.0	Compression set, 22hr/70°C, % set	40
Sulfur	1.5		

Heat Aging, 70 hr/70°C

Hardness/Tensile/Elongation changes +4/-10%/-18%

Heat Aging, 70 hr/100°C

Hardness/Tensile/Elongation changes +6/-16%/-39%

IRM 903 Oil Aging, 70 Hr/100°C

Hardness/Tensile/Elongation changes +1/-24%/-33%

Volume Change, % +1.0

*TSE-xxx is Tensile Stress at xxx% elongation ("modulus")



33 Shore A Non-Black Roller Compound

		XP-8266-F	Press Cured Properties, Cured 17 min/150°C	
Millathane® 76-65 (or -55)	75.0	Hardness Shore A	33	
Millathane CM-45 (or -55)	25.0	TSE-100*, psi (MPa)	95	(0.7)
Zinc Stearate	0.5	TSE-300*, psi (MPa)	290	(2.0)
Wacker HDK-N20	5.0	Tensile strength, psi (MPa)	1740	(12.0)
Silquest A-189	0.3	Elongation, %	655	
Akrofax 758	15.0	Tear Die C, lb/in (kN/m)	93	(16.3)
DBEEA (TP-95)	32.0	Tear Die B, lb/in (kN/m)	98	(17.2)
Millstab™ P	1.5	DIN Abrasion, mm ³ loss	173	
AC617A Polyethylene	1.0	Compression set, 22hr/70°C, % set	48	
MBTS	4.0	Bashore Resilience, %	45	
MBT	2.0			
Thanecure® ZM	1.0			
Sulfur, 80% active	2.3			

*TSE-xxx is Tensile Stress at xxx% elongation ("modulus")

Contact:

For further information or compound recommendations, visit our web site at www.millathane.com or email us at millathaneinfo@tse-industries.com.

Ingredients	Description	Supplier/Manufacturer
AC617A	Low molecular weight polyethylene	Honeywell
Akrofax 758	Sulfur-less vulcanized vegetable oil (factice)	Akrochem
Benzoflex 9-88SG	Dipropylene glycol dibenzoate	Eastman Chemical
Cabosil M-5	Fumed silica, surface area 200 m ² /g	Cabot Corporation
DBEEA (TP-95)	Di (butoxy-ethoxy-ethyl) adipate	Hallstar
Di-Cup 40C	Dicumyl Peroxide, 40%	Arkema Inc.
Irganox 1010	Antioxidant	BASF
Mediaplast NB-5	Adipic acid plasticizer (phthalate-free)	Kettlitz-Chemie
Millstab P**	Polymeric carbodiimide hydrolysis stabilizer	TSE Industries
Naugard 445	Antioxidant	Addivant
Si69	Silane Coupling Agent	Evonik
Silquest A189, A172, RC1	Silane Coupling Agents	Momentive Performance Materials
SR231, SR297, SR350	Liquid methacrylate coagents	Sartomer
Struktol AW-1	Antistatic plasticizer	Struktol Corporation
Struktol WB-222	Process aid	Struktol Corporation
Thanecure ZM	MBTS/Zinc chloride complex	TSE Industries
Ultrasil VN3	Precipitated silica	Evonik
Vanfre AP-2	Process aid	Vanderbilt Chemicals
Varox DBPH-50	2,5-Dimethyl-2,5-di(t-butylperoxy)hexane, 50%	Vanderbilt Chemicals
Wacker HDK N20	Fumed silica, surface area 200 m ² /g	Wacker Silicones

**Millstab P is sold, primarily in the USA, by TSE Industries. Other similar products, available worldwide, are Stabaxol P from Rhein Chemie and Stabilizer 2000/9000 from Raschig