



Millathane® 5004 and Millathane 5004M (Premilled*)

Millathane 5004 is a peroxide-curable millable polyurethane rubber used for production of parts for many applications including seals, gaskets, rollers, and diaphragms. Millathane 5004 is known for its excellent oil and solvent resistance, along with high strength and abrasion resistance properties.

Product Description

Chemical Composition:	Synthetic rubber based on ester/MDI polyurethane
Specific Gravity:	Approximately 1.21
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-5004-W (Virgin)	50 - 70	White to off-white chunks	50 pounds (22.7 kg)
M-5004-M (Premilled*)	50 - 70	Off-white solid sheets	50 pounds (22.7 kg)

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

Processing

NOTE: The 'chunks' of Millathane 5004-W may have a slippery feel, due to a very small amount of a mineral oil partitioning agent used in its manufacture. If this causes difficulties in mill mixing, adding a small amount of the filler that is in the formulation (e.g., silica) with the Millathane 5004-W when first adding it to the mill generally eliminates the problem. Alternatively, the Millathane 5004-W chunks can be cut (e.g., by a guillotine) to expose fresh surfaces which would be more easily banded on the mill.

Millathane 5004 is processed by techniques which are common to the rubber industry. Compounds can be mixed on open mills or in internal mixers. Molded articles can be produced via compression, transfer or injection molding. Injection molding Millathane 5004 provides very short cycle times, excellent flow and demolding and shows negligible mold fouling. Due to the peroxide vulcanization and its chemical base, Millathane 5004 can not be cured in direct contact with open steam or hot air, and, hence, for applications like hose, its use is limited to inner liners. Calendered sheets can be press-cured or Rotocured.

By its nature, Millathane 5004 is somewhat 'nervy' (tough), so compounds may not mill or calender as smoothly as other polymers, like Millathane 66. Millathane 66 can be blended with Millathane 5004 in any proportion to modify processing characteristics or modify properties.

Properties

Vulcanizates based on Millathane 5004 can be produced in hardnesses ranging from approximately 40 to 95 Shore A, and offer very good abrasion resistance, excellent oil resistance, good low temperature properties and good resistance to gas permeability.



Applications

The excellent balance of properties of Millathane 5004 makes it a perfect choice for various rubber parts including seals, gaskets, O-rings, suction cups, molded electrical parts, dust covers, mounts and bearings for the automotive industry and for many other hydraulic or pneumatic applications.

Compounding

Reinforcing Fillers

Reinforcing fillers like N330 carbon black or precipitated silica increase the mechanical strength of Millathane 5004 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 RC-1 or Dynasylan 6498, added at about 2% of the mineral filler content, generally improve tear strength, abrasion resistance and compression set.

Plasticizers

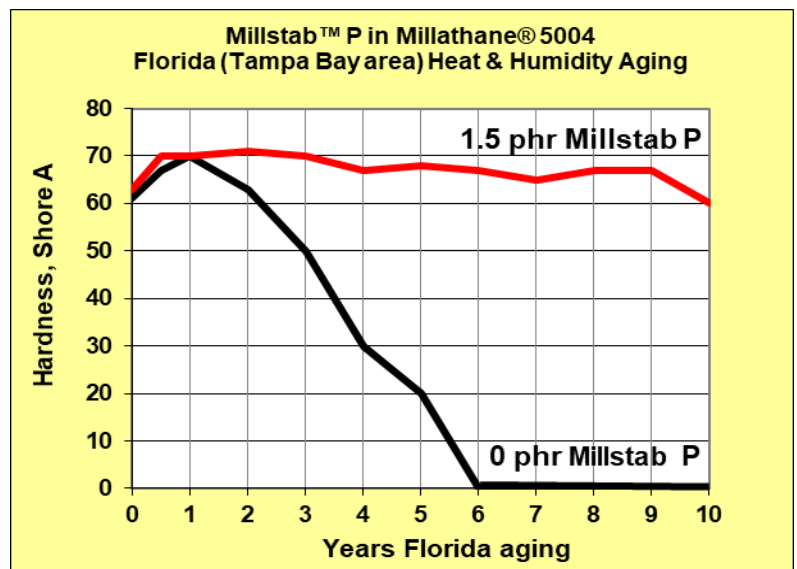
TP-95 (DBEEA) is a plasticizer that is very compatible with Millathane 5004, with compounds containing 25 phr and more usually not showing signs of bleeding or incompatibility. Other plasticizers such as Medioplast NB-4 and Benzoflex 9-88SG can also be used to plasticize and soften compounds. The antistatic 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.

Stabilizers/Antidegradants

Millathane 5004, 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 5004, which contains 1.5 phr of Millstab P, is a convenient way to include that amount of stabilizer in the compound, and it improves shelf stability of the polymer as well.

The chart to the right shows the benefit of 1.5 phr Millstab P to the Florida aging of a Millathane 5004 compound; the compound with Millstab P didn't soften at all, while the compound without Millstab P softened considerably at 3+ years, and fell apart after 5 years.

1 phr each of the antioxidants Naugard 445 and Naugard XL-1 can improve (slightly) the heat aging characteristics of Millathane 5004 compounds.





Process Aids

Small amounts of process aids are normally used to prevent sticking to processing equipment and to improve flow during molding. Generally, about 0.2 phr of stearic acid is used along with 0.5-2 phr of another process aid such as Struktol WB222 or Vanfre AP-2. Since stearic acid, and acids in general, tend to promote the effect of hydrolysis, it is recommended to keep its level very low. 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: Peroxides and Coagents

Typical peroxides used are Di-Cup and Varox DBPH-50, typically used at about 1.5 – 2.5 phr active peroxide. The use of coagents such as triallyl cyanurate (TAC) and trifunctional methacrylates like SR350 (TMTPMA) increase the crosslink density and improve compression set. Liquid methacrylates also function as non-extractable plasticizers. For high hardness compounds, blends of trifunctional and difunctional methacrylates (e.g. SR231, DEGDMA) give a good balance of tensile strength, elongation and good processing.

Vulcanization Conditions

Compounds based on Millathane 5004 are molded at temperatures of 140° - 180°C, depending on the peroxide, dimensions of the part etc. Injection molded parts with a wall thickness of less than 2 mm can be vulcanized in approximately one minute at 170° - 180°C mold temperature. 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 guidance in roller compounding and manufacture!

70 Shore A Black Molding Compound

(meets ASTM D2000 M4BG728 A14 B14 C12 EA14 EO34)

Table with 3 columns: Ingredient, Amount, and Property. Rows include Millathane 5004, Stearic acid, Millstab P, N 330 black, DBEEA, Struktol WB-222, Di-Cup 40 C, and various mechanical properties like Hardness, Tensile strength, Elongation, Tear Die C, and Compression set.

Heat Aging, 70 hr/100°C

Hardness/Tensile/Elongation changes +5/-32%/-5%

IRM 903 Oil Aging, 70 Hr/100°C

Hardness/Tensile/Elongation changes -5/-2%/+1%
Volume Change, % +0.7

Water Aging, 70 Hr/100°C

Hardness/Tensile/Elongation changes -6/-20%/+12%
Volume Change, % +1.4

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



73 Shore A Non-Black Molding Compound

(Would meet ASTM D2000 M4BG728 B14 EO34)

Millathane® 5004 Premilled	101.5	Press Cured Properties, Cured 4 min/170°C	
Stearic acid	0.2	Hardness Shore A	73
Ultrasil VN3	25.0	TSE-100, psi (MPa)	495 (3.4)
Silquest Y-15866	0.5	TSE-300, psi (MPa)	1770 (12.2)
DBEEA (TP-95)	5.0	Tensile strength, psi (MPa)	4060 (28.0)
Struktol WB-222	1.0	Elongation, %	490
Di-Cup 40 C	5.0	Tear Die C, lb/in (kN/m)	235 (41.1)
		Tear Die B, lb/in (kN/m)	310 (54.3)
		DIN Abrasion, mm ³ loss	98
		Compression set, 22hr/100°C, % set	34
		Surface resistivity, ohm/cm ²	5 x 10 ¹⁰
		Coefficient of Friction, kinetic (20# copy paper), µk	1.55

*TSE-xxx = 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
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.
Dynasylan 6498	Vinyl silane	Evonik
Irganox 1010	Antioxidant	BASF
Mediaplast NB-4	Adipine acid plasticizer	Kettlitz-Chemie
Millstab P**	Polymeric carbodiimide hydrolysis stabilizer	TSE Industries
Naugard 445, XL1	Antioxidants	Addivant
Silquest RC-1	Silane Coupling Agents	Momentive
SR231	Diethyleneglycol Dimethacrylate (DEGDMA)	Sartomer
SR350	Trimethylol propane Trimethacrylate (TMPTMA)	Sartomer
Struktol AW-1	Antistatic plasticizer	Struktol Corporation
Struktol WB-222	Process aid	Struktol Corporation
Tinuvin 328, 765	UV stabilizers	BASF
TP-95	Di (butoxy-ethoxy-ethyl) adipate (DBEEA)	Hallstar
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 in the US by TSE Industries. Other similar products, available worldwide, are Stabaxol P from Rhein Chemie and Stabilizer 2000/9000 from Raschig

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