

Millathane® CM

Millathane CM, originally developed by DuPont in the late 1950's as Adiprene* C (later, Adiprene CM), is a sulfur or peroxide curable polyether millable polyurethane rubber with excellent physical properties and abrasion resistance. It also has good oil resistance and excellent low temperature properties, and is used for molded articles, rollers and military and aircraft applications.

Product Description

| Chemical Composition: | Synthetic rubber based on Ether/TDI polyurethane |
|-----------------------|---|
| Specific Gravity: | Approximately 1.06 |
| Storage stability: | 3 years from date of manufacture (stored under dry and cool conditions) |

| Part Number | Mooney Viscosity MS(1+10)/100°C** | Appearance | Package size/carton |
|-------------|--------------------------------------|-------------------------------|---------------------|
| M-00CM-40 | 35 – 45 | Orange to tan solid sheets | 50 pounds (22.7 kg) |
| M-00CM-45 | 40 – 50 | Orange to tan solid sheets | 50 pounds (22.7 kg) |
| M-00CM-55 | 50 – 60 | Orange to tan solid sheets | 50 pounds (22.7 kg) |

Processing

Millathane CM is processed by techniques which are common to the rubber industry: Compounds can be mixed on an open mill or in an internal mixer. Molded articles can be produced via compression, transfer or injection molding; calendered sheets can be press or Rotocured.

Properties

Vulcanizates based on Millathane CM can be produced in hardnesses ranging from about 30 to 95 Shore A, and offer high strength properties, excellent abrasion resistance, water resistance and good oil resistance. Compounds have low brittle points and have good resistance to stiffening at low temperatures, much better than Millathane E34, a similar polymer.

Applications

Because of its low temperature properties and high abrasion resistance, Millathane CM finds use in military and commercial aircraft applications including wing deicing bladders and dust covers. Millathane CM is also used for belts, bushings, seals, rollers and other applications that need the excellent combination of properties it can provide.

Compounding

Reinforcing Fillers

Reinforcing fillers like N330 carbon black or silicas (precipitated or fumed) are commonly used to increase the hardness and mechanical strength of Millathane CM compounds. Larger particle size blacks like N550 and N774, and other fillers, including clay, talc and calcium carbonate can also be used to modify properties and processing, but are less reinforcing than silicas and blacks. Silicas, talcs and clays are commonly used with silane coupling agents to improve properties

* Adiprene is a registered trademark of Chemtura

** Note: ML(1+4) values would be approximately double the MS(1+10) values (e.g., 40 MS(1+10) would be approximately 80 ML(1+4)).

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Coupling Agents

Silane coupling agents like Silquest A-189 or Si 69 for sulfur cures, or Silquest RC-1 or Silquest A172 for peroxide cures, will generally improve the tear strength, abrasion resistance and set properties of silica reinforced compounds and are typically used at about 2% of the mineral filler content.

Plasticizers

TP-95 is a plasticizer that is very compatible with Millathane CM, with compounds containing 25 phr or more will usually not show signs of bleeding or incompatibility. Other plasticizers such as Mediaplast 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.

Antidegradants

Polyurethanes are generally very resistant to ozone and oxygen attack because of their saturated polymer backbones (like EPDM). Small amounts (0.5-2 phr) of antioxidants like Naugard 445 and Irganox 1010 can provide some benefit to the heat aging characteristics of peroxide-cured Millathane CM 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 that is used as an activator is often 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 use in place of the zinc stearate. A low molecular weight polyethylene like AC617A, added at 1-4 phr, gives good release for calendering and molding.

Curing Agents

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. Peroxide cures can be used for better set and heat aging characteristics, at some expense of physical properties. 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 (TMTPMA) increase the crosslink density and improve compression set of peroxide cures. Blends of the difunctional methacrylates, like SR231 (DEGDMA) with the trifunctional methacrylate SR350 can be used at higher levels 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 Millathane CM compounds are typically molded at temperatures of 150° - 165°C; higher temperatures can give poor cures due to reversion. Peroxide-cured compounds can be cured from 145°-175°C, depending on the peroxide, dimensions of the part etc. Rubber covered rollers are often cured in steam or electric autoclaves, under pressure, at 135°-150°C for 1-6 hours (very large rolls for longer times at lower temperatures), depending on the compound and roll geometry. Protection from direct contact with steam is necessary.



Formulation Examples

48Shore A Non-Black Molding or Roller Compound, Sulfur Cured

| Millathane® CM | 100.0 | Mooney Viscosity, ML(1+4)/100°C | 35 | |
|-----------------------------|-------|--|------|--------|
| Zinc Stearate | 0.5 | | | |
| Ultrasil VN3 | 5.0 | Press Cured Properties, Cured 17 min/150°C | | |
| Natro-Cel BCA-A (72% DBEEA) | 30.0 | Hardness Shore A | 48 | |
| Akrofax 11LG | 10.0 | TSE-100, psi (MPa) | 130 | (0.9) |
| Struktol WB-222 | 1.0 | TSE-300, psi (MPa) | 320 | (2.2) |
| MBTS | 4.0 | Tensile strength, psi (MPa) | 2895 | (10.0) |
| MBT | 2.0 | Elongation, % | 710 | |
| Thanecure® ZM | 1.0 | Tear Die C, lb/in (kN/m) | 135 | (23.6) |
| 80% Sulfur Dispersion | 2.0 | Tear Die B, Ib/in (kN/m) | 142 | (24.9) |
| | | Bashore Resilience, % | 46 | |
| | | DIN Abrasion, mm ³ loss | 54 | |

65 Shore A Non-Black Molding Compound, Sulfur Cured

| Millathane® CM | 100.0 | Mooney Viscosity, ML(1+4)/100°C | 65 | |
|-----------------|-------|--|------|--------|
| Zinc Stearate | 0.5 | | | |
| Ultrasil VN3 | 25.0 | Press Cured Properties, Cured 18 min/155°C | | |
| Silquest A189 | 0.5 | Hardness Shore A | 65 | |
| TP-95 (DBEEA) | 5.0 | TSE-100, psi (MPa) | 325 | (2.2) |
| Struktol WB-222 | 1.0 | TSE-300, psi (MPa) | 1310 | (9.0) |
| MBTS | 4.0 | Tensile strength, psi (MPa) | 4500 | (31.0) |
| MBT | 2.0 | Elongation, % | 525 | |
| Thanecure® ZM | 1.0 | Tear Die C, lb/in (kN/m) | 239 | (40.3) |
| Sulfur | 1.5 | Bashore Resilience, % | 45 | |
| | | Compression set, 22hr/70°C, % set | 54 | |
| | | DIN Abrasion, mm ³ loss | 51 | |

87 Shore A Black Molding Compound, Sulfur Cured

| Millathane® CM | 100.0 | Mooney Viscosity, ML(1+4)/100°C | 126 | |
|-----------------|-------|---|------|--------|
| Zinc Stearate | 0.5 | | | |
| N220 Black | 60.0 | Press Cured Properties, Cured 6 min/160°C | | |
| Cumar P-25 | 7.0 | Hardness Shore A | 87 | |
| AC617A | 2.0 | TSE-100, psi (MPa) | 1100 | (7.6) |
| Struktol WB-222 | 1.0 | TSE-300, psi (MPa) | 3160 | (21.8) |
| MBTS | 4.0 | Tensile strength, psi (MPa) | 3660 | (25.2) |
| MBT | 2.0 | Elongation, % | 410 | . , |
| Thanecure® ZM | 1.0 | Tear Die C, lb/in (kN/m) | 299 | (52.3) |
| Sulfur | 1.5 | Tear Die B, lb/in (kN/m) | 615 | (108) |
| | | Bashore Resilience, % | 32 | |
| | | Compression set, 22hr/70°C, % set | 33 | |
| | | DIN Abrasion, mm ³ loss | 92 | |

Please visit our web site (<u>www.tse-industries.com</u>) for additional formula examples or contact us (<u>millathaneInfo@tseind.com</u>) for specific formula recommendations for your application

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Adhesion to Metal

Millable polyurethanes generally have very good adhesion to metal, and adhesives from several manufacturers give excellent bonding. Below are results of testing done by adhesive manufacturers on bonding a sulfur-cured, silica reinforced Millathane E34 (similar to Millathane CM) compound to steel. Note that the testing was done by the three different companies under different conditions with probably different steel grades and different test sample preparation and adhesion test protocols, so the test results should only be used as a guide to recommended adhesives and should not be used as a direct comparison between the adhesives.

| Adhesive | Adhesion | Failure |
|-------------------------------------|-----------------------|---------------------|
| Ty-Ply BN ¹ | 111 lb/in [19.4 N/mm] | Rubber Failure 100% |
| Chemlok 218 ¹ | 128 lb/in [22.4 N/mm] | Rubber Failure 100% |
| Cilbond 49SF+Cilcure B ² | 115 lb/in [20.2 N/mm] | Rubber Failure 100% |
| Thixon 715-1/720:MEK 1:13 | 106 lb/in [18.6 N/mm] | Rubber Failure 100% |

Other adhesives that have been used successfully and/or recommended for use for bonding to metal are: Chemlok 213¹, Chemlok 218¹ and Chemlok 219¹ for bonding to Aluminum and steel Chemlok 250¹ and Thixon³ 405 for bonding during injection molding. Cilbond 89ET² and Cilbond 12E/80ET² Megum 15637³, Megum 508 and Megum 3276

¹Lord Corporation,²Chemical Innovations Ltd. (CIL), ³Dow Chemical

Additional Information

Visit our web site (<u>www.tse-industries.com</u> or <u>www.millathane.com</u>) for information on Millathane CM and other Millathane grades, as well as technical studies, TIPS and SDS documents, and other information. Inquiries can be sent to <u>millathaneInfo@tseind.com</u>.

| Ingredients | Description | Supplier/Manufacturer |
|----------------------------|---|---------------------------------|
| AC617A | Low molecular weight polyethylene | Honeywell |
| Akrofax 11LG | Factice (Vulcanized Vegetable Oil) | Akrochem |
| Benzoflex 9-88SG | Dipropylene glycol dibenzoate | Eastman Chemical |
| Cumar P-25 | Coumarone Indene Resin (liquid) | Neville Chemical |
| Irganox 1010 | Antioxidant | BASF |
| Mediaplast NB-4 | Adipine acid plasticizer | Kettlitz-Chemie |
| Natro-Cel BCA-A | 72% DBEEA | Natrochem |
| Naugard 445 | Antioxidant | Addivant |
| Si 69 | Silane Coupling Agent | Evonik |
| Silquest RC-1, A172, A-189 | Silane Coupling Agents | Momentive Performance Materials |
| 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 |
| TAC (Vanlink TAC) | Triallyl cyanurate | Vanderbilt Chemicals |
| Thanecure® ZM | MBTS/zinc chloride complex | TSE Industries, Inc. |
| TP-95 | Di (butoxy-ethoxy-ethyl) adipate (=DBEEA) | Hallstar |
| Ultrasil VN3 | Precipitated silica | Evonik |
| Vanfre AP-2 | Process aid | Vanderbilt Chemicals |

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