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Technical Information for Performance Solutions

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Isocyanate Cures of Millathane® Compounds

Typical cure systems used with millable polyurethanes are the sulfur cure system and the peroxide cure system. The typical sulfur cure system is a combination of MBTS, MBT, Thanecure® ZM and sulfur (with zinc stearate as an activator). A typical peroxide cure system includes the peroxide and often a coagent. There is another cure system that can be used with some grades of millable polyurethane: the isocyanate cure system. This consists of dimerized TDI (Thanecure® T9SF), HQEE or another low molecular weight polyol, along with a small amount of an accelerator.

A rough comparison of the physical characteristics of these three cure systems is shown below:

Cure System	Sulfur	Peroxide	Isocyanate
Hardness range (typical), Shore A	30-90	40-95	70-98
Properties, Low Hardnesses (<60A)	Very Good	Fair-Good	N/A
Properties, Med Hardnesses (60-80A)	Excellent	Very Good	Very Good
Properties, High Hardnesses (>80A)	Very Good	Good/Very Good	Excellent
Abrasion Res, High Hardnesses	Good	Fair-Good	Excellent
Shelf life, compound	Good	Very Good	Poor

As indicated, isocyanate cures get excellent properties and abrasion resistance at high hardnesses, with the main disadvantage being the short shelf life. The shelf life of polyester grades can be very short (about 1 day at room temperature), so compounds needing to be used after that time need to be stored in freezer or refrigerator. Isocyanate cures of several polyether Millathane grades, however, have been shown to have improved shelf life, being still moldable for 3 days/RT.

Applications

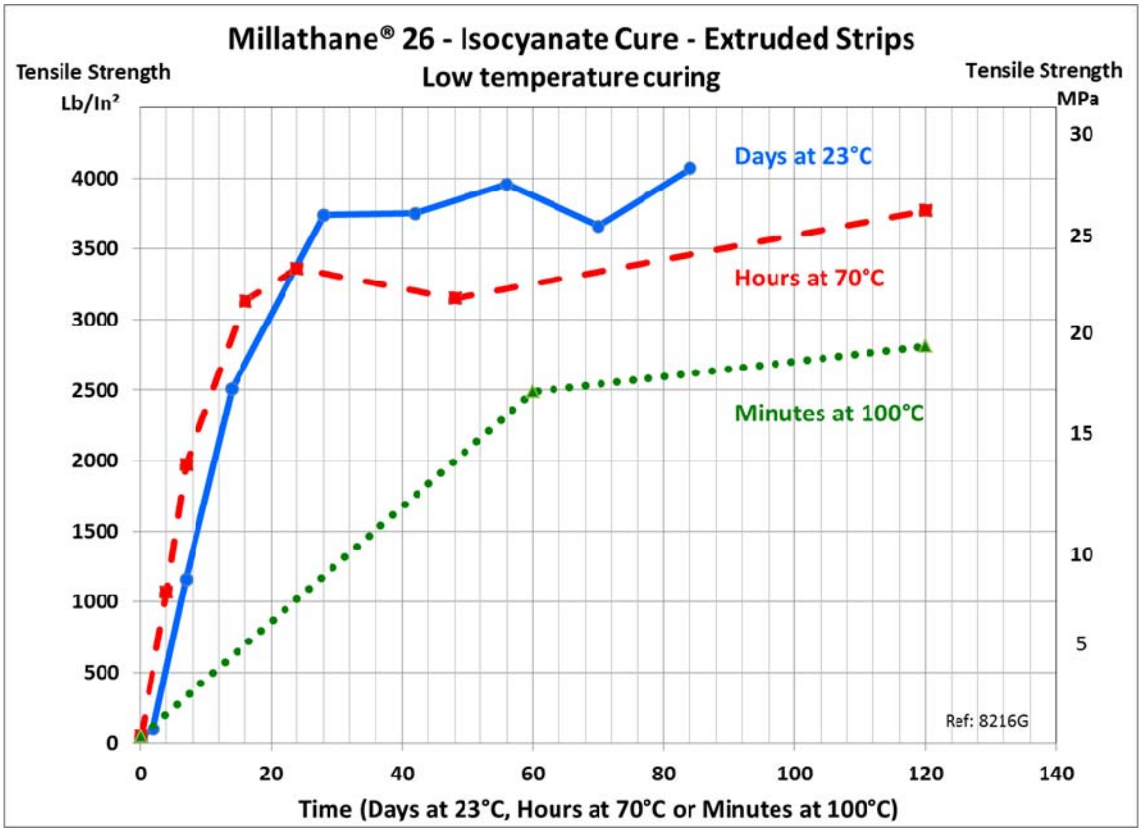
High hardness isocyanate-cured millable polyurethane compounds have been used for many years in the ceramic tile industry, for making molds to press and form clay mixtures into tiles which are later baked or fired in an oven. These rubber-covered molds use high hardness compounds with high strength and high abrasion resistance. Various other molded parts requiring high strength and abrasion resistance at high hardnesses also use the isocyanate cure system with millable polyurethanes.

Processing and Vulcanization

Isocyanate-cured Millathane compounds are typically mixed on rubber mills, with stearic acid added with the polymer at the very beginning of the mix to prevent mill sticking. Mills should be kept cool to minimize mill sticking. Internal (e.g., Banbury®) mixing is not normally recommended due to the heat buildup of millable urethanes and the potential for sticking and premature vulcanization (scorching). After mixing, compounds should be slabbed off and allowed to air-cool. Mixed compounds have very limited shelf life because of the isocyanate cure system, and must be used within 1-3 days of mixing (See section on Shelf Stability). Storage life can be extended by storing the compound at low temperatures, -5ºC to +5ºC.

Molded articles are typically produced via compression molding at temperatures of 120º - 135ºC (higher temperatures are not recommended) for 15 – 25 minutes, with thick articles taking correspondingly longer times.

Millathane compounds using the isocyanate cure system can also be cured at relatively low temperatures or even at room temperature (about 20º - 25ºC). A study was done with a Millathane 26 compound containing 20 phr of Thanecure® T9SF, 6.8 phr of HQEE, 0.3 phr of Bismate and 1 phr of Irganox 1076. This compound was extruded into a thin strip and strips cured at room temperature (23° C), 70°C and 100°C for various times and then tested for tensile strength. The chart below shows that the compound cured very well in about 60-120 minutes at 100°C, in 24 hours at 70°C or in 28 days at room temperature. This low temperature curing capability would potentially be useful for applications such as tank linings and outdoor sheeting.

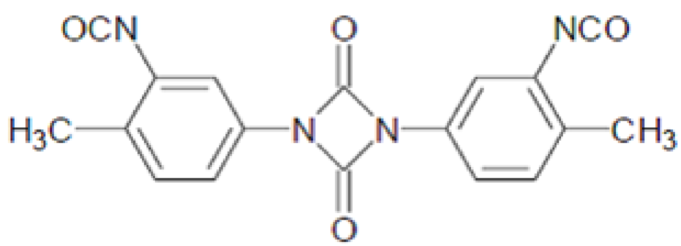


Compounding

Typical compounds contain little more than the polymer, the cure system, as described above, and a process aid. Ingredients are:

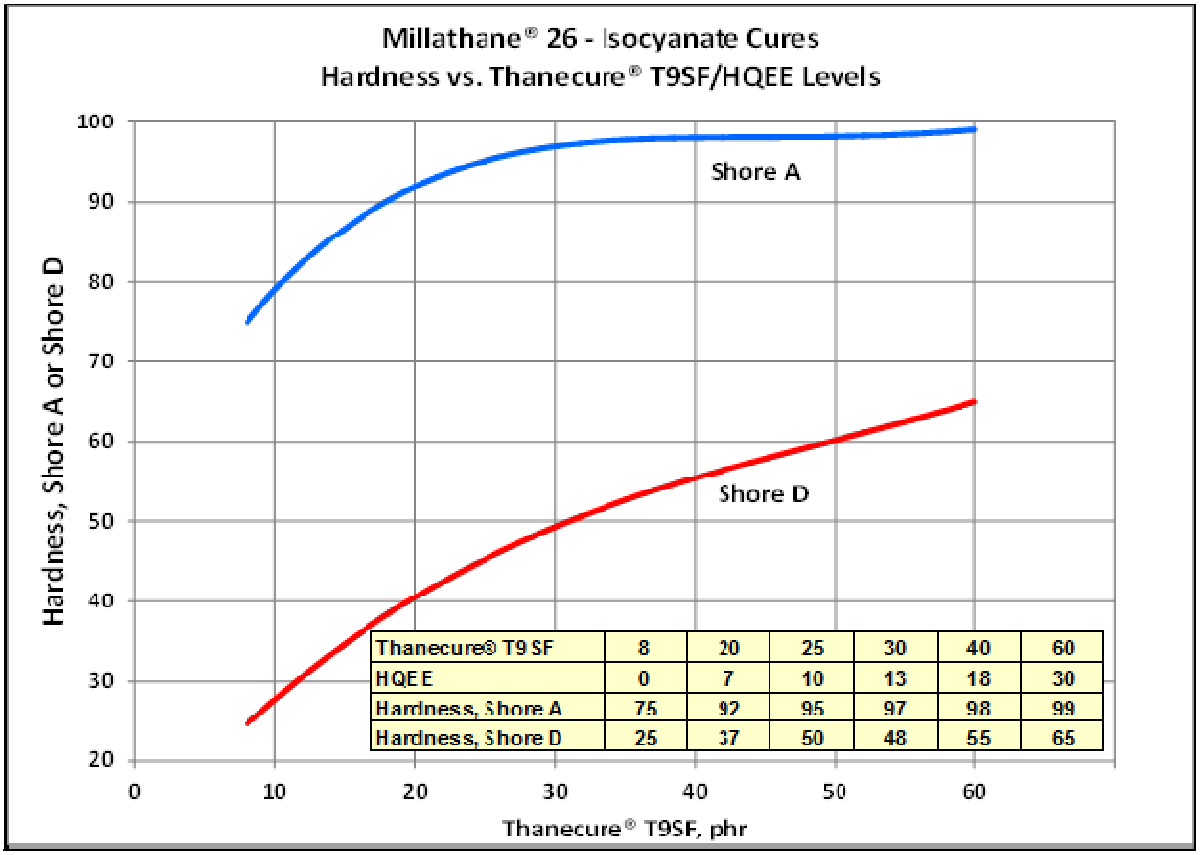
Millable Polyurethane – Not every Millathane grade can be vulcanized with the isocyanate cure system. Grades that give good properties with this cure system are Millathane 26 (best!), Millathane E34, Millathane 55, Millathane 97 and Millathane 76. Low viscosity grades are usually desirable as they generate less heat during mixing, which can affect scorch and shelf life of the compounds.

Dimerized TDI (TDI Dimer) – Thanecure® T9 SF – is the main component of the cure system, and is typically used at levels ranging from about 7 to about 40 phr. Thanecure T9 SF is a finely ground powder and should be stored under cool and dry conditions. For critical applications, the material can be screened (sieved) through fine mesh (200 mesh) screens.



Thanecure® T9SF (TDI Dimer)

Diol or glycol, like HQEE – HQEE (HydroQuinone bis(2-hydroxylEthyl) Ether) – is a crosslinking agent used with Thanecure T9SF. The amount of HQEE used is approximately 57% of the amount of Thanecure T9SF over 8 phr of Thanecure T9SF. So, for 20 phr of Thanecure T9SF, approximately 6.8 phr of HQEE should be used ([20-8]*0.57). The chart on the next page shows the effect of Thanecure T9SF and HQEE levels on cured hardness.



HQEE is somewhat moisture sensitive and should be kept in closed containers in a cool, dry place. If it has absorbed moisture, drying at 75°-80°C in an oven (vacuum oven, preferably) can remove that moisture. HQEE used for vulcanizing millable polyurethane should be finely ground and sieved (200 mesh screens) before using, or it must be melted into the polymer in a separate step. A masterbatch of Millathane® 26, HQEE flake (e.g., Poly-G HQEE), and stearic acid, mixed at 105°C for 3 minutes, worked well.

An alternative material to HQEE is a low molecular weight polyol such as Terathane® PTMEG 250. This material has the advantage of being a liquid so it doesn't have the potential problem of poor dispersion. A comparison in the table below shows that Terathane 250 gave a little better tensile strength, compression set and Taber abrasion resistance, compared to the other two HQEEs, although the hardness, tensile stress ('modulus') and tear strength were somewhat lower. All three compounds had *outstanding* DIN abrasion results (26-27 mm³ loss).

	9450-A	9450-B	9450-D
Millathane® 26	100	100	100
Stearic Acid	0.5	0.5	0.5
Thanecure® T9SF	25	25	25
HQEE (ground)	**9.7**	—	—
Poly-G HQEE (flake)*	—	**9.7**	—
Terathane 250	—	—	**9.7**
Bismate	0.3	0.3	0.3

* fluxed with the Millathane 26 and stearic acid in a separate step

Press Cure, 20 minutes at 130°C

Hardness, Shore A/Shore D	95/47	95/48	89/40
TSE-100*, lb/in² (MPa)	995 (6.9)	1010 (7.0)	755 (5.2)
TSE-300*, lb/in² (MPa)	1400 (9.7)	1390 (9.6)	1230 (8.5)
Tensile Strength, lb/in² (MPa)	3500 (24.1)	4420 (30.5)	5320 (36.7)
Elongation, %	620	715	585
Tear, Die C, lb/in (kN/m)	477 (84)	468 (82)	385 (67)
Tear, Die B, lb/in (kN/m)	479 (84)	473 (83)	399 (70)

Bashore Resilience, %	58	57	56
Compression Set, 22 hr/70°C, %	45	46	29
DIN Abrasion, mm³ loss**	27	27	26
Taber Abrasion Index***	41	48	36

*TSE-xxx=Tensile Stress at xxx% Elongation

**ASTM D5963 Test Method B (rotating test piece)

*** ASTM G195, H-18, wheels, 1 kg weight, mg loss/1K cycles (5K cycle test)

Accelerator – This has historically been PbDMC (lead dimethyldithiocarbamate) but this product has been discontinued due to health and other concerns. BiDMC (bismuth dimethyldithiocarbamate, 'Bismate') performs similarly to PbDMC. It is a yellow powder and will give yellowish vulcanizates, although a small amount of titanium dioxide will minimize the yellowness. Very limited testing with ZDBC, zinc dibutydithiocarbamate, indicates that it may also function similarly in this cure system. These accelerators are typically used at 0.1-0.5 phr.

Process Aids – Stearic acid is typically used at 0.3-0.5 phr. A low melting polyethylene like AC1702 can be added (1-2 phr) for improved mill and mold release.

MILLATHANE® FACTOID: *TSE Industries will be at the DKT (German Rubber) show in Nuremberg, Germany, July 2-4, 2018, at the booth of our European distributor Safic-Alcan. Stop in if you have any millable polyurethane questions.*

Other additives – A small amount of silicone fluid (e.g., 1 phr of DF55-1000) can be added to improve abrasion resistance, although it should be carefully evaluated for applications that require adhesion to metal or another substrate. Low levels of silica (e.g., Ultrasil V3) and plasticizer (DBEEA, TP-95) can be used to modify properties.

Shelf Stability – As noted previously, the isocyanate cure system yields very short shelf life compounds, due to the reactivity of the TDI Dimer at low temperatures. Evaluations of the shelf life of compounds made of two Millathane grades, 26 and 55, showed, however, that they had much better shelf life than a competitive isocyanate-cured millable polyurethane. Data in the table below and the pictures of the cured samples indicate that the competitive compound molded very poorly after 3 days at room temperature, while the two Millathane-based compounds molded very well. The Tangent Delta (TD) values after aging, and the change from the original values, suggest that the competitive material would be more difficult to mold after aging (lower TD indicates more "nerviness" of the compounds, and often poorer molding).

Millathane® grade	26	Competitive*	55
Tangent Delta at ML (MDPt, 130°C)			
Original	0.9	0.6	1.3
Aged 3 days/23°C	0.6	0.4	1.1
% change	-36	-41	-15
Aged 7 days/23°C	0.5	0.3	0.9
% change	-36	-56	-26
Tensile sheet appearance, cured after aging uncured compounds as noted			
Original (molded after mixing)	Excellent	Excellent	Excellent
Compound aged 3 days/23°C	Excellent	Poor-Speckled	Very Good

Cured sheet à

*Competitive isocyanate-cured millable polyurethane

MILLATHANE® FACTOID: If you missed Tom Jablonowski's paper at the IEC (International Elastomer Conference) in Cleveland last October, on improved adhesion of millable polyurethane to other rubber types, it will be published in an upcoming issue of Rubber & Plastics News.

Typical Compounds Using the Isocyanate Cure System

	7596D	8216E	9470C	8201L	7527A	8262A
Millathane® Grade at 100 phr	**26**	**26**	**55**	**76**	**26**	**26**
Stearic Acid	0.3	0.3	0.3	0.5	0.3	0.5
Thanecure® T9SF	8.0	20.0	20.0	20.0	25.0	60.0
HQEE (ground)	—	—	6.8	7.0	9.7	30.0
Terathane 250	—	8.5	—	—	—	—
Bismate (BiDMC)	0.5	0.3	0.3	0.6	0.3	0.3
Ultrasil VN3	5.0	—	—	—	—	—
DBEEA	3.0	—	—	—	—	—
Irganox 1076	—	1.0	—	—	—	—
Akrocal 80	—	3.0	—	—	—	—
Physical Properties, Press Cure 20 min/130ºC						
Hardness, Shore A	72	87	93	94	95	99
Hardness, Shore D	—	35	38	37	50	65
TSE-100*, lb/in²	335	860	940	755	1100	2900
MPa	2.3	5.9	6.5	5.2	7.6	20
TSE-300*, lb/in²	405	1350	1235	960	1835	3680
MPa	2.8	9.3	8.5	6.6	12.7	25.4
Tensile Strength, lb/in²	3570	6100	2900	3210	7500	5010
MPa	24.6	42.1	20	22.1	51.7	34.6
Elongation, %	850	560	710	805	530	445
Tear Die C, lb/in	206	360	336	342	403	810
kN/m	36	63.0	59	60	70	141
Tear Die B, lb/in	410	390	—	310	540	1140
kN/m	72	68.3	—	54	94	199
DIN Abrasion, mm³ loss	41	36	71	25	36	89
Bashore Resilience, %	67	54	53	39	55	65
Compression Set, 22 hr/70°C, %	—	32	—	44	47	—

Ingredients	**Description**	**Supplier**
A-C® 1702	Polyethylene homopolymer	Honeywell
Akrocal 80	Calcium oxide, 80%	Akrochem
Bismate® (BiDMC)	Bismuth dimethyldithiocarbamate	Vanderbilt Chemicals
DF55-1000	Silicone (PDMS) fluid, 1000 cs	Akrochem
Irganox 1010	Antioxidant	BASF
Millathane® 26, 55, 97, E34	Polyether millable polyurethanes	TSE Industries, Inc.
Millathane® 76	Polyester millable polyurethane	TSE Industries, Inc.
Poly-G HQEE®	Hydroquinone bis(2-hydrolxethyl)ether	Monument Chemical
Terathane® PTMEG 250	Polytetramethylene ether glycol, 250 MW	Invista
Thanecure® T9SF	TDI Dimer	TSE Industries, Inc.
TP-95® (DBEEA)	Dibutoxyethoxyethyl adipate	Hallstar
Ultrasil® VN3	Precipitated silica	Evonik

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ASK Doctor Millathane®

Dear Dr. Millathane,

I have an application that requires parts that are 2 inches thick. Any comments on molding thick parts of Millathane® millable polyurethane?

Dick Gummi

Dear Dick,

Generally, curing thick articles requires extending cure times, for heat transfer to cure the interior of the part, and very often reducing cure temperatures, to minimize the difference in cure state between the exterior and the interior of the part. The latter is especially important with rubber types that can revert (diminish in properties upon over-curing), like natural rubber and millable polyurethanes.

Peroxide cures of millable PU are usually much less reverting than sulfur cures, so for peroxide cures it may just be necessary to extend the cure time. We press-cured 2” x 2” x 6” (5 mm x 5 mm x 15 mm) samples using two different compounds. A peroxide-cured Millathane 26 compound cured for 26 minutes at 160°C (rheometer test at 160°C showed a tc90 of 7 minutes) and it was evenly cured throughout. A sulfur-cured Millathane E34 compound which had a tc90 of 4.5 minutes at 177°C and 350 minutes at 120°C cured well with 50 minutes at 145°C.

For curing thick sections, it’s best to check the curing with a rheometer test at the intended cure temperature and give additional cure time for thicker sections (we generally add 5 minutes to the tc90 for every ½” (1.3 cm) of thickness). If the rheometer curve shows significant reversion for the estimated cure time, temperature should be reduced, and cure time increased, to minimize over-curing of the part’s exterior.

Dr. Millathane

If you have any Millathane millable urethane questions you’d like answered, please send an email to millathaneinfo@tse-industries.com.