



Antioxidants in Millathane® 26

Millathane® 26 is a polyether millable polyurethane that was developed primarily for food handling applications, and it complies with the U.S. FDA regulation 21CFR177.2600. Because of its excellent properties, it also finds its way into many applications not requiring FDA compliance including rollers, belting and hoses.

Being a polyether polyurethane, Millathane 26 has only fair heat resistance, definitely not as good as polyester polyurethanes such as Millathane 66. Antioxidants, however, can significantly improve heat aging characteristics. This study looks at various combinations of the two antioxidants Irganox 1010¹ and Naugard 445². Note that neither of these antioxidants are FDA-compliant³, so for food handling applications, Irganox 1076⁴ can be used. Also, note that Naugard 445 is somewhat discoloring and staining, especially in sunlight; Irganox 1010 and 1076 are not discoloring or staining.

EXPERIMENTAL

Masterbatches were first mixed, containing either 0 or 2 phr of the two antioxidants, and these masterbatches were then blended, along with peroxide, to get the various antioxidant combinations of the formula below.

Compounds were tested for curing behavior, cured properties (tensile slabs cured to tc90, thicker samples t90+5'), abrasion resistance (DIN Abrasion, ASTM D5963, Method B), compression set resistance (per ASTM D395 Method B, solid samples) and heat resistance (ASTM D 573).

	XP-7591
Millathane® 26	100.00
Stearic Acid	0.20
N330 Black	25.00
TP-95 (DBEEA)	2.00
Struktol WB 222	1.00
SR-350 (TMPTMA)	2.00
Irganox 1010	0 – 2
Naugard 445	0 – 2
DiCup 40C	5.00

CURING CHARACTERISTICS

The addition of the antioxidants had a slight effect in lengthening the scorch time (ts1, 160°C MDR) and cure time (tc90), with N445 having more of an effect than AO1010, but the differences were slight.

ORIGINAL PROPERTIES

The cured properties of both compounds were negligibly affected by the antioxidants. All compounds tested 57 Shore A durometer and had tensile strengths of 19.8-22.0 MPa (2875-3190 lb/in²). Tear strength and compression set properties were not significantly affected by the antioxidants. DIN Abrasion was slightly better with compounds having equal amounts of the two antioxidants and the compound without antioxidants.

I-1010	0	0.5	1	0	1	2	0
N-445	0	0.5	0	1	1	0	2
Press Cure, t90 at 160° C							
Hardness, Shore A	57	57	57	57	57	57	57
TSE-100*, psi (MPa)	175 (1.2)	170 (1.2)	160 (1.1)	180 (1.2)	180 (1.2)	170 (1.2)	170 (1.2)
TSE-300*, psi (MPa)	635 (4.4)	625 (4.3)	560 (3.9)	665 (4.6)	690 (4.8)	585 (4.0)	605 (4.2)
Tensile Strength, psi (MPa)	3000 (20.7)	3080 (21.2)	3000 (20.7)	3190 (22.0)	3180 (21.9)	3170 (21.9)	3035 (20.9)
Elongation, %	730	745	775	740	705	800	760
Tear, Die C, lb/in (kN/m)	172 (30.1)	172 (30.1)	170 (29.8)	179 (31.3)	167 (29.2)	172 (30.1)	179 (31.3)
Tear, Die B, lb/in (kN/m)	320 (56.0)	306 (53.6)	321 (56.1)	308 (53.9)	311 (54.4)	302 (52.9)	311 (54.4)
DIN Abrasion, mm ³ loss (rotating)	84	83	91	87	82	90	89

*TSE-xxx = Tensile Stress at xxx% Elongation



Antioxidants in Millathane® 26 (cont.)

AGING PROPERTIES

Compression Set

The addition of the antioxidants did not have a significant effect on compression set.

Heat Resistance

Compounds were tested for physical properties after oven exposures of 70 hours at 70°C, 100°C and 125°C. The results, tabulated below and plotted (tensile strength change only) showed:

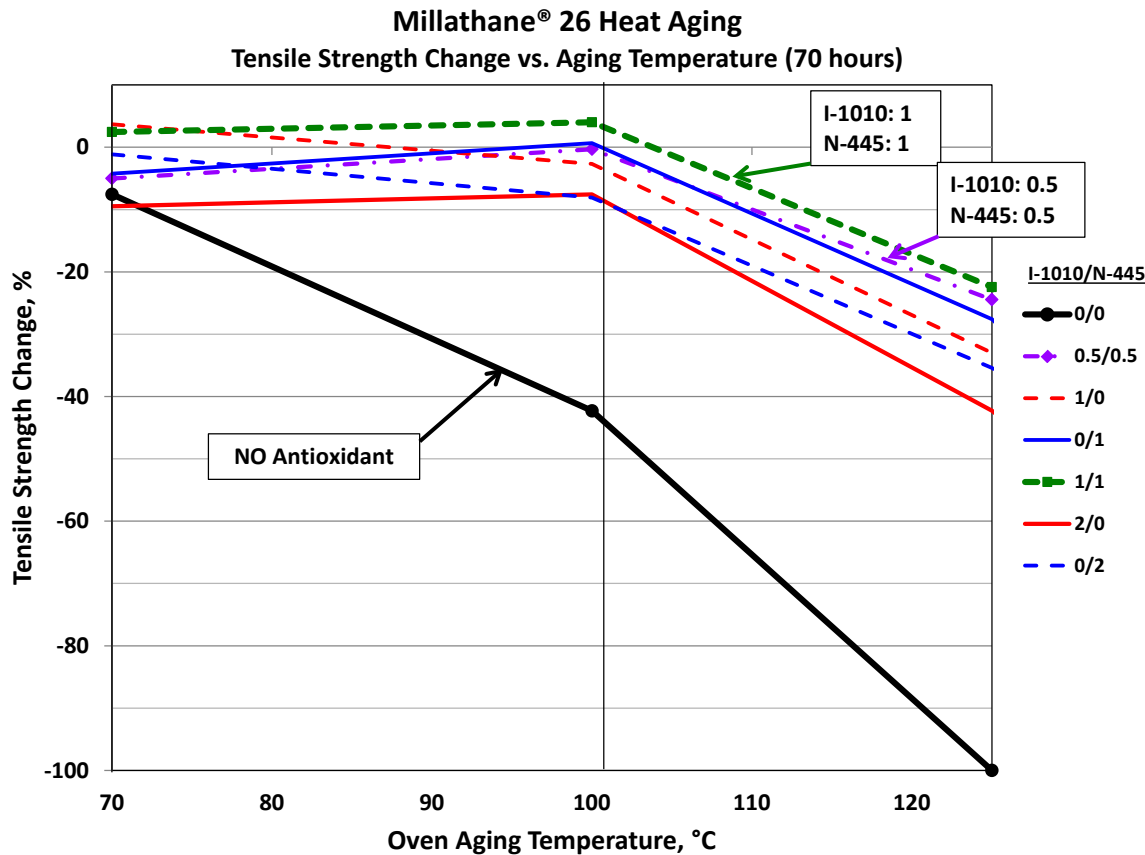
- **70°C Aging:** All compounds had excellent retention of properties, with negligible changes in any property.
- **100°C Aging:** The compound with no antioxidant had significant losses of tensile (-42%) and elongation (-30%), but all of the other compounds, with 1-2 phr of antioxidant, had very minimal changes in properties.
- **125°C Aging:** The compounds with equal amounts of Irganox 1010 and Naugard 445 (0.5 or 1.0 phr each) had the least change in tensile and elongation; the other compounds containing antioxidants had higher losses of tensile and elongation. The compound with no antioxidant lost 100% of its strength properties.

I-1010	0	0.5	1	0	1	2	0
N-445	0	0.5	0	1	1	0	2
Compression Set, % Set							
22 hr / 70°C	30	32	35	32	30	32	34
22 hr / 100°C	54	52	55	53	51	51	53
22 hr / 125°C	87	88	89	89	84	88	92
Oven Aged 70 hr / 70°C							
Hardness Change, Shore A	0	0	0	0	0	0	0
Tensile Strength Change, %	-8	-5	4	-4	2	-9	-1
Elongation Change, %	-3	-3	-1	-3	-3	-9	1
Oven Aged 70 hr / 100°C							
Hardness Change, Shore A	0	0	0	0	0	0	0
Tensile Strength Change, %	-42	0	-3	1	4	-8	-8
Elongation Change, %	-30	2	-5	-9	-6	-13	-9
Oven Aged 70 hr / 125°C							
Hardness Change, Shore A	-57	-5	-7	-6	-5	-6	-5
Tensile Strength Change, %	-100	-24	-33	-28	-22	-42	-35
Elongation Change, %	-100	-24	-33	-28	-22	-42	-35

¹Tetrakis [methylene (3,5-di-tert-butyl-4-hydroxy hydrocinnamate)] methane; Irganox 1010 (BASF) and Songnox 1010 (Songwon) are comparable. ²4,4'-Bis (alpha, alpha-dimethylbenzyl) diphenylamine; Naugard 445 (Addivant) and Vanox CDPA (Vanderbilt) are comparable. ³For food contact, per 21CFR 177.2600. ⁴Octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate; Irganox 1076 (BASF) and Songnox 1076 (Songwon) are comparable.



Antioxidants in Millathane® 26 (cont.)



SUMMARY

- A low level of antioxidant (0.5-2.0 phr) in peroxide-cured Millathane® 26 is very beneficial to heat aging (as it is in other polyether polyurethanes).
- The amine antioxidant Naugard 445 gives better heat resistance than the phenolic antioxidant Irganox 1010, and blends of the two are synergistically better than either antioxidant individually.
- A similar study was done with the polyester polyurethane Millathane 66. Because polyester polyurethanes are inherently better for heat aging than polyether grades, the antioxidants did not have any significant effect on aging characteristics.
- Studies with sulfur-cured Millathane® compounds have shown that antioxidants are not beneficial to their heat aging properties.
- A small amount (~0.25 phr) of antioxidant is necessary for all Millathane® 97 compounds and is highly recommended for all Millathane® 26 compounds.

The recommendations for the use of our products are based on tests believed to be reliable. However, we do not guarantee the results to be obtained by others under different conditions. Nothing in this literature is intended as a recommendation to use our products so as to infringe on any patent. Millathane® and Thanecure® are registered trademarks of TSE Industries, Inc.