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Technical Information for Performance Solutions

Antioxidants in Millathane® 26

Introduction

Millathane 26 is a polyether Millable polyurethane that was developed primarily for food handling applications, and it complies with the US FDA regulation 21CFR177.2600. Because of its excellent properties, it also find 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 1010[1] and Naugard 445[2]. Note that neither of these antioxidants are FDA-compliant[3], so for food handling applications, Irganox 1076[4] 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.

Topics:

Experimental

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

	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

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).

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/in^2). Tear strength and compression set properties were, likewise, 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.

[1] Tetrakis[methylene(3,5-di-tert-buryl-4-hydroxy hydrocinnamate)]methane; Irganox 1010 (BASF) and Songnox 1010 (Songwon) are comparable.
[2] 4,4'-Bis(alpha, alpha-dimethylbenzyl) diphenylamine; Naugard 445 (Addivant) and Vanox CDPA (Vanderbilt) are comparable.
[3] For food contact, per 21CFR 177.2600.
[4] Octadecyl 3,5-di-tert-butyl-4-hydroxyhyrocinnamate; Irganox 1076 (BASF) and Songnox 1076 (Songwon) are comparable.

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	175	170	160	180	180	170	170
MPa	1.2	1.2	1.1	1.2	1.2	1.2	1.2
TSE-300, psi	635	625	560	665	690	585	605
MPa	4.4	4.3	3.9	4.6	4.8	4.0	4.2
Tensile Strength, psi	3000	3080	3000	3190	3180	3170	3035
MPa	20.7	21.2	20.7	22.0	21.9	21.9	20.9
Elongation, %	730	745	775	740	705	800	760
Tear, Die C, lb/in	172	172	170	179	167	172	179
kN/m	30.1	30.1	29.8	31.3	29.2	30.1	31.3
Tear, Die B, lb/in	320	306	321	308	311	302	311
kN/m	56.0	53.6	56.1	53.9	54.4	52.9	54.4

*TSE-xxx=Tensile Stress at xxx% Elongation

DIN Abrasion, mm³ loss (Rotating)	84	83	91	87	82	90	89

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.

MILLATHANE® FACTOID: The addition of 1 phr of Naugard 445 to a Millathane 97 compound solved a cracking problem of the part that was exposed, after curing, to 1 hr/ 175°C.

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/70ºC

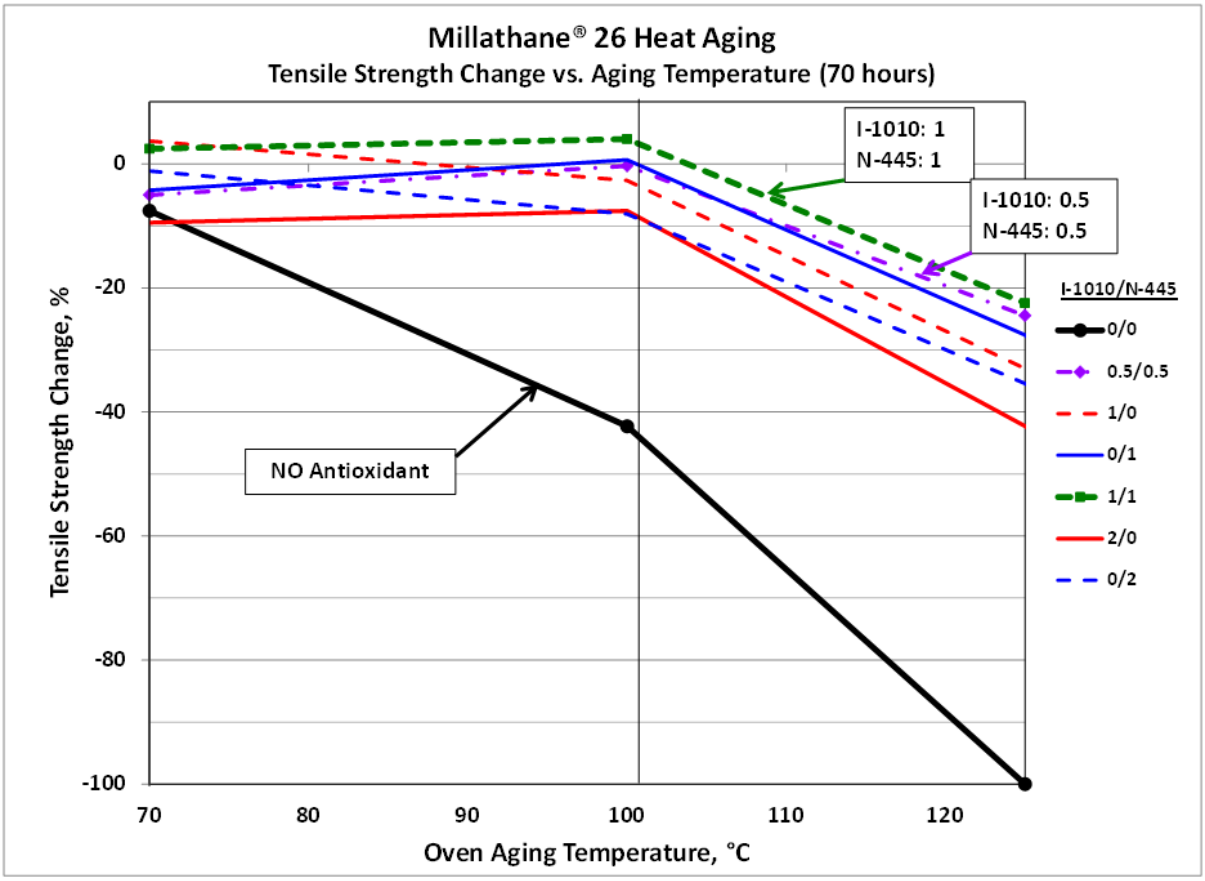
Hardness Change, Shore A	0	0	0	0	0	0	0
Tensile Strength Change, %	-8	-5	4	-4	2	-9	-1
Elongation Change, %	-3	-3	-1	-3	-3	-9	1

Oven Aged 70 hr/100ºC

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/125ºC

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



Summary and Comments on Antioxidants in Millathane 26 (and other Millathane Grades)

1. 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).

2. 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.

3. A similar study was done with the polyester polyurethane Millathane 66, and, because polyester polyurethanes are inherently better for heat aging than polyether grades, the antioxidants did not have any significant effect on aging characteristics.

4. Studies with sulfur-cured Millathane compounds have shown that antioxidants are not beneficial to their heat aging properties.

5. A small amount (~0.25 phr) of antioxidant is necessary for all Millathane 97 compounds and is highly recommended for all Millathane 26 compounds. See our Millathane 97 bulletin for the best Antioxidant and UV Stabilizer recommendations.

MILLATHANE® FACTOID: *Hydrophobic fumed silicas, like Cabosil TS-720, give much more resistance to water absorption than precipitated silicas.*

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ASK Doctor Millathane®

Dear Dr. Millathane,

I am curing a part from a pretty basic Millathane 26 formula, and the flash is very sticky and difficult to clean from the mold. Can you advise how to reduce the stickiness of the flash?
Maya Flashistuk

Dear Maya,

The flash of peroxide cured Millathane compounds, especially polyether grades like Millathane 26, can tend to be sticky because of inhibition of the peroxide curing agent from exposure to atmospheric oxygen. Adding a small amount (0.25—0.5 phr) of an antioxidant should solve the problem.

Good Luck!
Dr. Millathane

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