

Technical Information for Performance Solutions

Millathane® 5004 Blends with Hydrin® H1100 for Oxidized Fuel Resistance

Epichlorohydrin elastomers are frequently used in automotive applications such as hoses, diaphragms and gaskets because of their good oil, fuel and heat resistance along with excellent resistance to gas permeability and good low temperature properties. A study was conducted by Zeon Chemicals* to evaluate a blend of Hydrin H1100, a polyepichlorohydrin (CO), with Millathane 5004, a polyester millable urethane (AU), to try to improve the sour (oxidized) fuel resistance of the CO. Although there are several cure systems that can be used with Hydrin H1100, the peroxide cure system was used for compatibility with the peroxide curable Millathane 5004.

Topics:

- Millathane® 5004 Blends with Hydrin® H1100 for Oxidized Fuel Resistance
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Formulation

The formulas used were as shown below, being identical for the two polymers except for the hydrolysis stabilizer Millstab™ P added to the Millathane 5004 compounds. The 50:50 blend compound was made by blending the 100% Hydrin H1100 and 100% Millathane 5004 compounds.

Hydrin® H1100	100.00	50.00	—
Millathane® 5004	—	50.00	100.00
N550	20.00	20.00	20.00
N330	20.00	20.00	20.00
Mistron® CB	10.00	10.00	10.00
Paraplex® G50	10.00	10.00	10.00
Stearic Acid	0.25	0.25	0.25
Struktol® WB222	2.00	2.00	2.00
Maglite® D	5.00	5.00	5.00
Vanox® CDPA	1.00	1.00	1.00
Vanox® MTI	1.00	1.00	1.00
Millstab™ P	—	1.00	2.00
Varox® 802-40KE	5.00	5.00	5.00

Rheometrics

Curemeter (ODR) data showed the Millathane 5004 compounds to have lower ML (viscosity) but higher MH (maximum torque). The cure and scorch characteristics were fairly similar. MDR data showed similar trends.

ODR, 20'/170°C (micro-die, 100 cpm, 3° arc)

ML, lbf-in	9.6	3.6	2.8
dNm	10.8	4.1	3.2
MH, lbf-in	39.4	39.6	59.1
dNm	44.5	44.7	66.8
ts2, minutes	2.1	2.1	2.0
t90, minutes	14.0	11.3	11.6

*Thanks to Sam Harber of Zeon Chemicals for conducting the study and to Zeon Chemicals for permission to publish this data.

The following are registered trademarks of the companies noted: Hydrin (Zeon Chemicals), Millathane (TSE Industries), Mistron (Rio Tinto Minerals), Paraplex and Maglite (HallStar), Struktol (Struktol Co.), Vanox and Varox (R.T. Vanderbilt). Millstab is a trademark of TSE Industries, Inc.

Physical Properties

In the standard formula used, the 100% Millathane 5004 compound tested significantly harder (74A vs. 54 A) than the 100% Hydrin H1100 compound, with tensile stress values also higher, in line with the hardness values. Tear strength of the Millathane 5004 compound was significantly higher than the Hydrin H1100 compound, with the 50:50 blend giving intermediate properties.

Original Properties, Press Cured 15'/170°C

	Hydrin H1100	50/50 Blend	Millathane 5004
Hardness, Shore A	54	66	74
TSE-100*, psi	366	509	607
MPa	2.5	3.5	4.2
TSE-200, psi	787	994	1183
MPa	5.4	6.9	8.2
TSE-300, psi	1156	1434	1737
MPa	8.0	9.9	12.0
Tensile Strength, psi	1577	1787	2548
MPa	10.9	12.3	17.6
Elongation, %	458	416	539
Tear, Die C, lb/in	198	214	330
kN/m	34.7	37.5	57.8

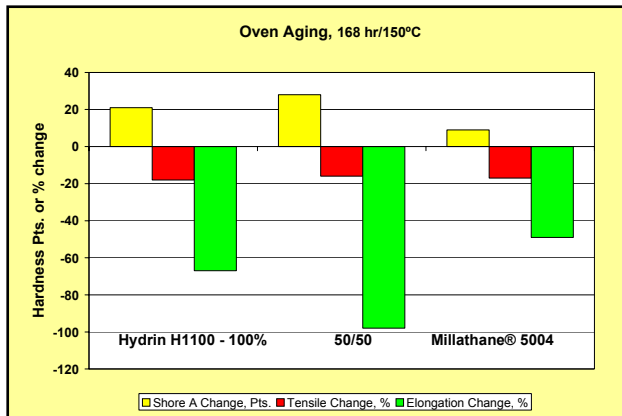
*TSE-XXX = Tensile Stress at XXX elongation

MILLATHANE® FACTOID:

Zinc oxide and calcium oxide have harmful effects on the curing of Millathane compounds, and contamination with these materials should be avoided.

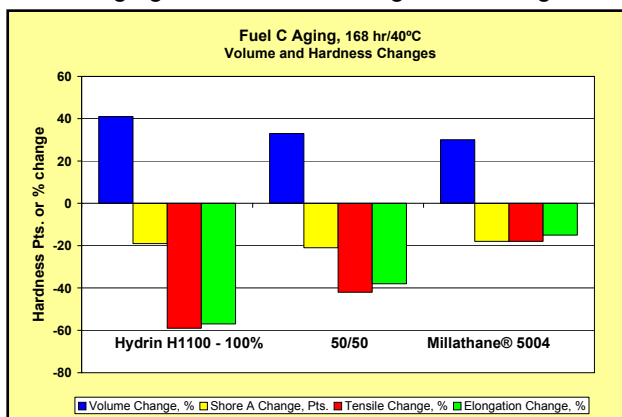
Oven Aging

Oven aging of the sample for 1 week at 150°C showed the 100% Millathane 5004 compound to be somewhat better for property retention vs. the 100% Hydrin H1100 compound, with the 50/50 blend of Hydrin H1100/Millathane 5004 being (unexpectedly) poorer than either polymer for hardness change and especially elongation change.



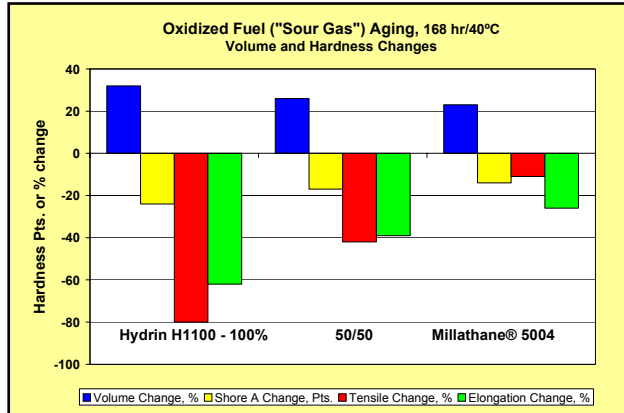
Fuel C Aging

Aging in ASTM Fuel C (a 50:50 blend of isooctane and toluene), a common test for rubber parts in contact with fuels, was also conducted on the blends. As the chart below shows, the addition of Millathane 5004 to the Hydrin H1100 improved the retention of hardness, tensile strength and elongation after the Fuel C aging, as well as reducing the swelling in the fluid.



Oxidized Fuel (Sour Gas) Aging

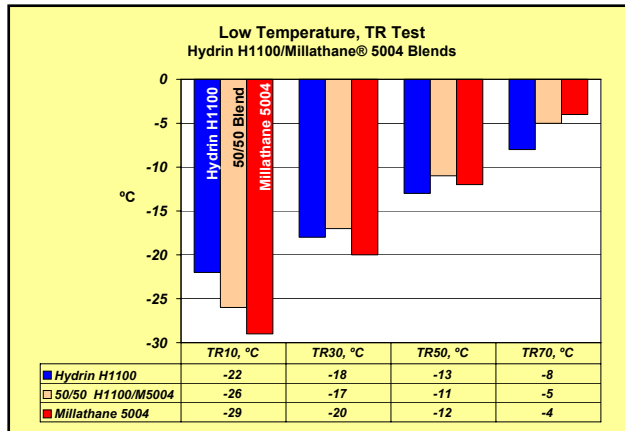
Testing for fuel exposure also typically includes testing in “sour gas” to simulate oxidized fuel. SAE J30, *Fuel and Oil Hoses*, specifies the composition of oxidized fuel as a mixture of 3600 ml ASTM Fuel B (a 70:30 blend of isooctane and toluene) and 10 ml of a 90% t-butyl hydroperoxide in water, producing a fuel mixture with a peroxide number of 50. The compounds in this study were immersed in this “sour gas” for 1 week at 40°C (without changing the fuel frequently as is specified in SAE J30). The results, in the chart below, show similar trends as with the Fuel C data, with better resistance to the “sour gas” as Millathane 5004 is added to the Hydrin H1100.



Low Temperature, TR Test

The low temperature TR test, ASTM D1329, evaluates the low temperature flexibility of rubber compounds. Per ASTM, the TR10 values correlate with brittle points and the TR70 values correlate with low temperature compression set. Also, the difference between TR10 and TR70 values suggests tendency to crystallize at low temperatures.

The data for the three compounds, shown below, indicate that the addition of Millathane 5004 to the Hydrin H1100 improved (lowered) the TR10 value, but decreased slightly the TR30, TR50 and TR70 values. This suggests that the Hydrin is more resistant to low temperature crystallization than Millathane 5004, although maybe with a higher temperature brittle point.



Summary

Peroxide-cured polyepichlorohydrin (Hydrin H1100) was blended with Millathane 5004 and the blends generally gave properties intermediate between those of the two polymers. Millathane 5004 and the Millathane 5004/Hydrin H1100 gave, vs. 100% Hydrin H1100:

- * Higher hardness and tensile stress (modulus), in the same formula
- * Slightly improved original strength properties (tensile and tear strengths)
- * Better Fuel C and oxidized fuel (“sour gas”) resistance
- * Slightly better TR10 values, but slightly poorer TR70 values (TR30 and TR70 values were similar)
- * Better 150°C oven aging for 100% Millathane 5004, although the 50/50 blend with Hydrin H1100 was poorer than the other compounds.

Abrasion resistance would also be expected to be better for the Millathane 5004-containing compounds. Blending these two polymers, or possibly using 100% Millathane 5004, is a tool that can be useful for applications requiring good resistance to fuels and sour gas such as automotive or off-the-road applications.

MILLATHANE®
FACTOID: A small amount of Irganox 1076 (0.5 phr) greatly improves the heat aged properties of Millathane 26 compounds, giving minimal property changes after 100°C aging.

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ASK Doctor Millathane®

Dear Dr. Millathane,

Can I make transparent articles with Millathane compounds?

Crystal C. Lear

Dear Crystal,

For transparent articles, it is strongly recommended to use Millathane 97 which was designed for transparency, originally for transparent athletic shoe soles. In compounding Millathane 97, you also need to use ingredients that will not hurt the transparency:

- * Fumed silica for reinforcement (e.g., Wacker HDK N20 or Aerosil 200)
- * Clear plasticizers, if necessary (e.g., Kettlitz Medioplast NB-4)
- * Antioxidants and UV (ultraviolet light) stabilizers (e.g., Irganox 1010 and Tinuvin 328 and Tinuvin 765), and
- * Neat (not on carriers) peroxides (e.g., Luperox 231 or Varox DCP-R).

Our Millathane 97 brochure, found on the download page of our web site, gives further information and our recommendations for formulating Millathane 97 compounds.

Other polymers can be formulated similarly, but because of their composition, they would not be as transparent originally nor would they maintain their transparency as well over time as Millathane 97.

Dr. Millathane

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