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.

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'/170ºC (micro-die, 100 cpm, 3º arc)			
ML, lbf-in (dNm)	9.6 (10.8)	3.6 (4.1)	2.8 (3.2)
MH, lbf-in (dNm)	39.4 (44.5)	39.6 (44.7)	59.1 (66.8)
ts2, minutes	2.1	2.1	2.0
t90, minutes	14.0	11.3	11.6

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'/170ºC	**Hydrin® H1100**	**50/50 Blend**	**Millathane® 5004**
Hardness, Shore A	54	66	74
TSE-100*, psi (MPa)	366 (2.5)	509 (3.5)	607 (4.2)
TSE-200*, psi (MPa)	787 (5.4)	994 (6.9)	1183 (8.2)
TSE-300*, psi (MPa)	1156 (8.0)	1434 (9.9)	1737 (12.0)
Tensile Strength, psi (MPa)	1577 (10.9)	1787 (12.3)	2548 (17.6)
Elongation, %	458	416	539
Tear, Die C, lb/in (kN/m)	198 (34.7)	214 (37.5)	330 (57.8)

**TSE-XXX = Tensile Stress at XXX Elongation*

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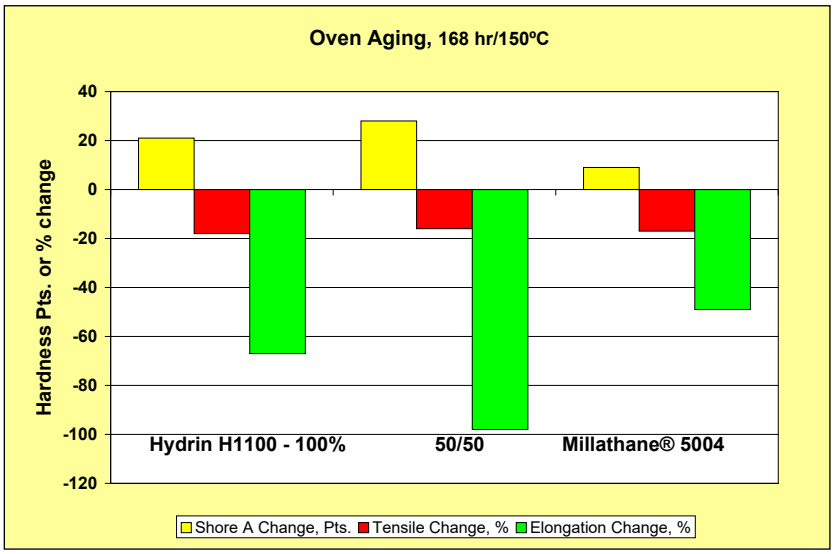
Millathane® 5004 Blends with Hydrin® H1100 (cont.)

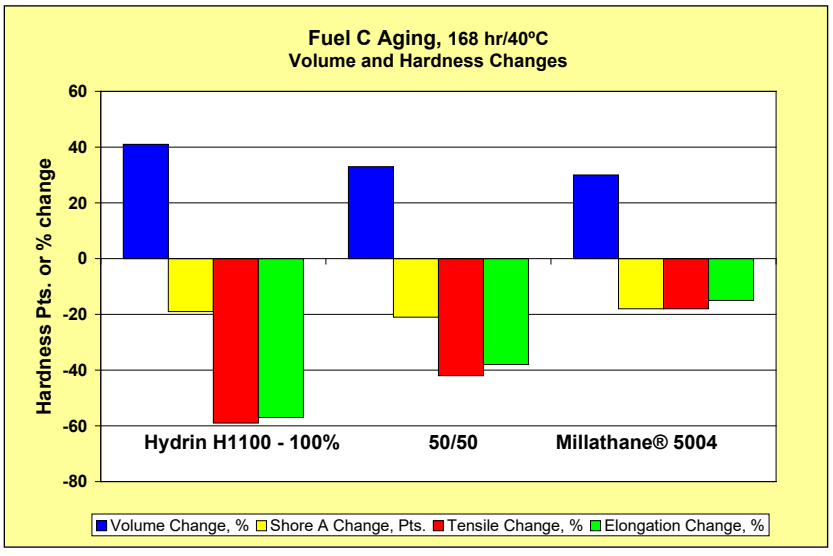
OVEN AGING

Oven aging of the sample for one week at 150ºC 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 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.



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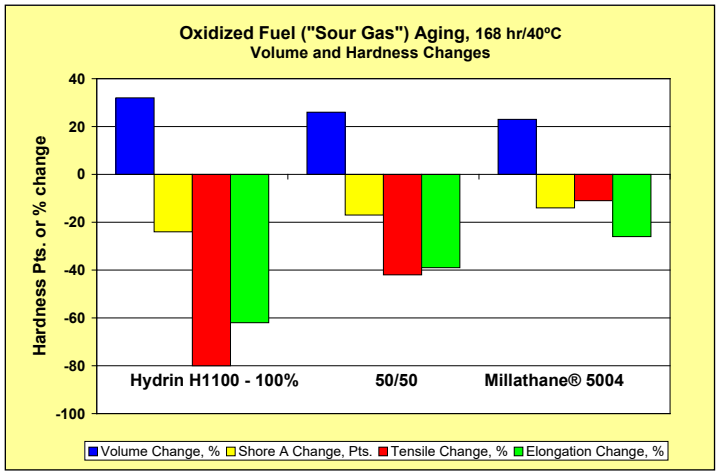
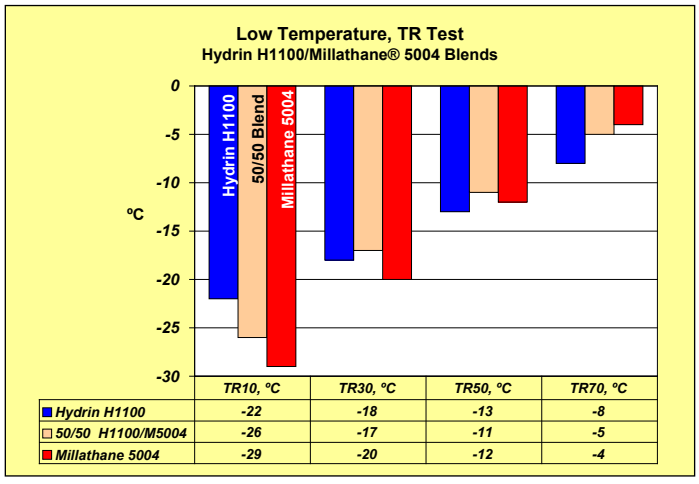
OXIDIZED FUEL (SOUR GAS) AGING

Testing for fuel exposure 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 “sour gas” for one week at 40ºC (no change the fuel frequently as is specified in SAE J30). The results show similar trends as with the Fuel C data, with better resistance to the “sour gas” as 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. The difference between TR10 and TR70 values suggests tendency to crystallize at low temperatures. The data for the three compounds indicate that the addition of Millathane® 5004 to the Hydrin® H1100 improved (lowered) the TR10 value, but decreased the TR30, TR50 and TR70. This suggests that Hydrin® is more resistant to low temperature crystallization than 5004, although maybe with a higher temperature brittle point.



	TR10, °C	TR30, °C	TR50, °C	TR70, °C
Hydrin H1100	-22	-18	-13	-8
50/50 H1100/M5004	-26	-17	-11	-5
Millathane 5004	-29	-20	-12	-4

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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 150ºC 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% 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.

**Thanks to Zeon Chemicals for conducting the study and permission to publish the data. The following are registered trademarks of the companies noted: Hydrin (Zeon Chemicals), Millathane and Millstab (TSE Industries), Mistron (Rio Tinto Minerals), Paraplex and Maglite (HallStar), Struktol (Struktol Co.), Vanox and Varox (R.T. Vanderbilt).*

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