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Plasticizers For Hypalon®

Ten plasticizers were tested for general performance characteristics in Hypalon® 40 compounds vulcanized using a magnesia/peroxide/co-agent cure system. The plasticizers examined were as follows, with an unplasticized compound serving as a control:

Plasthall® 83SS	Plasthall® P-7068
Plasthall® DOS	Plasthall® P-7092
Plasthall® DBES	Monoplex® S-75
Plasthall® CF	Paraplex® G-62
Plasthall® P-670	

Conclusions

1. Plasthall® 83SS provided excellent plasticizing efficiency, original and post air aging low-temperature flexibility and permanence following immersion in ASTM 1 and 3 Oil.

2. Monoplex® S-75 provided mid-range efficiency and original low-temperature flexibility, along with excellent volatility and distilled water extraction resistance.

3. Plasthall® DBES and DOS (and to a lesser extent, CF) provide excellent efficiency and original low-temperature flexibility but lack volatility resistance and permanence following immersion in ASTM 1 Oil.

4. Polymeric polyesters, Plasthall® P-670 and P-7092, are well suited for applications requiring excellent permanence and low-temperature flexibility maintenance following fuel and oil immersion.

5. Plasthall® P-7092 provides unusually low Hypalon® 40 compound viscosities.

Experimental

Hypalon® is a chlorosulfonated polyethylene of which the sulfonyl chloride groups provide highly reactive sites for cross-linking. The recipe used in this work employs a magnesia/peroxide/co-agent cure system designed to provide processing safety and good compression set resistance. The peroxide used was 6 PPHR of Vul-cup 40KE and 5.6 PPHR of TAC co-agent absorbed onto an inert silica at a 72 percent activity level. The Maglite® D magnesium oxide serves as an acid acceptor and also a cross-linking agent by providing weak ionic bonds. Pentaerythritol assists by promoting cure along with the magnesium oxide. Plasticizers were added at 30 PPHR, which corresponds to 14 percent of the compound. Hypalon® 40 is considered by DuPont to be their general-purpose chlorosulfonated PE and has a chlorine content of 35 percent and sulfur content of 1.0 percent.

Plasticizer performance was examined by testing the following physical properties:

Viscosity and Curing	Compression Set
Original Physicals	Immersions:
Roll Spew	Fuel B/Dry Out
Low-Temperature Impact/Gehman	Distilled Water/Dry Out
Air Oven Aging	ASTM I Oil
	ASTM 3 Oil

Summary

Results indicate that Monoplex® S-75 would serve well as a good "work horse" plasticizer requiring broad performance properties. Plasthall® 83SS should be considered for its excellent efficiency, original low-temperature flexibility and flexibility maintenance following air-oven aging. Polymeric polyesters, Plasthall® P-670 and P-7092, should be useful for maximizing permanence in fuels and oils while maintaining low-temperature flexibility following these immersions.

900130

Recipe EN03-132	1	3	4	5	6	7	8	9	10	11
Recipe Variable	83SS	DOS	DBES	CF	S-75	P-670	P-7068	P-7092	G-62	Unplas

Data

Recipes for Banbury Mixing and Physical Testing

Recipe EN03-132	1	3	4	5	6	7	8	9	10	11
Hypalon® 40	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Maglite® D Powder	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Pe-1702 AC	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
N-774	55.0	55.0	55.0	55.0	55.0	55.0	55.0	55.0	55.0	55.0
Pe-200	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
1246 Wax	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Suprmix® Tac	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6
Plasthall® 83ss	30.0	-	-	-	-	-	-	-	-	-
Plasthall® DOS	-	30.0	-	-	-	-	-	-	-	-
Plasthall® DBES	-	-	30.0	-	-	-	-	-	-	-
Plasthall® CF	-	-	-	30.0	-	-	-	-	-	-
Monoplex® S-75	-	-	-	-	30.0	-	-	-	-	-
Plasthall® P-670	-	-	-	-	-	30.0	-	-	-	-
Plasthall® P-7068	-	-	-	-	-	-	30.0	-	-	-
Plasthall® P-7092	-	-	-	-	-	-	-	30.0	-	-
Paraplex® G-62	-	-	-	-	-	-	-	-	30.0	-
Sub Total	207.6	207.6	207.6	207.6	207.6	207.6	207.6	207.6	207.6	177.6
Mill Addition										
VUL-CUP 40KE	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
TOTAL	213.6	213.6	213.6	213.6	213.6	213.6	213.6	213.6	213.6	183.6

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Major Variable	83SS	DOS	DBES	CF	S-75	P-670	P-7068	P-7092	G-62	Unplas
Mooney Viscosity: at 135°C (275°F)										
Minimum Viscosity	13.1	9.0	9.1	10.2	10.6	12.5	6.2	1.1	13.0	46.2
t5, min	22.2	25.0	24.0	25.0	27.3	37.5	25.0	-	26.2	12.7
t35, min	-	-	-	-	-	-	57.2	-	-	37.7
Oscillating Disc Rheometer: at 182°C (360°F)										
ML, lbf/in	24.4	23.8	23.8	23.8	25.8	25.0	26.0	6.0	27.0	60.2
MH, lbf/in	56.1	90.8	66.8	91.0	87.0	105.6	113.8	118.0	100.0	-
ts2, min	3.3	2.5	2.4	2.7	2.5	3.5	2.7	3.5	2.5	1.9
t'c(90), min	9.5	9.4	9.5	9.7	9.1	9.7	8.3	9.5**	8.4	6.5*
Cure Rate Index	16.1	14.5	14.1	14.3	15.2	16.1	17.9	16.7	16.9	21.7
1.25 x tlc(90), min	11.9	11.8	11.9	12.1	11.4	12.1	10.4	11.9	10.5	8.1

*Cure Time was taken where the curve crossed the 200 lb.-in axis because the curve went off scale.
**Cure Time was not taken from the graph but was estimated.

Original Physical Properties										
Stress at 100% Elong., MPa	1.9	3.1	2.1	4.1	3.8	4.8	4.7	5.7	3.3	14.5
psi	275	450	300	600	550	700	675	825	475	2100
Stress at 200% Elong., MPa	4.5	8.6	5.3	10.0	8.6	11.7	10.9	-	8.6	-
Stress at 300% Elong., MPa	7.2	-	8.6	-	12.8	-	-	-	13.6	-
Tensile, Ultimate, MPa	11.2	12.8	11.0	12.9	13.1	14.8	15.9	15.3	14.1	22.1
psi	1625	1850	1600	1875	1900	2150	2300	2225	2050	3200
Elong. at Break, %	480	290	400	260	310	250	290	190	320	140
Hard., Duro A, pts.	61	63	61	64	65	69	67	71	67	81
Specific Gravity	1.308	1.288	1.301	1.290	1.297	1.328	1.317	1.335	1.311	1.376
Tear Resistance, ppi	178	139	168	136	158	139	151	132	162	140

Roll Spew Compatibility:

Temperature at 23°C, -1°C, -21°C										
Exudation through 96 h	None	None	None	None	None	None	None	None	None	None

Low-Temperature Impact:

As Molded,										
All Pass, °C	49	52	51	-49	-41	-35	-36	-29	-36	-23

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Recipe EN03-132 Recipe Variable	1 83SS	3 DOS	4 DBES	5 CF	6 S-75	7 P-670	8 P-7068	9 P-7092	10 G-62	11 Unplas
Low-Temperature Torsion Gehman: Original										
T_2, °C	-7	-12	-6	-12	-10	-10	-7	-8	-8	-6
T_5, °C	-24	-28	-25	-28	-24	-21	-20	-16	-20	-15
T_{10}, °C	-31	-35	-33	-34	-29	-26	-22	-20	-24	-17
T_{100}, °Cc	-42	-48	-47	-48	-38	-33	-32	-27	-32	-23
Apparent Modulus of Rigidity, psi	97	116	100	129	122	164	145	193	135	262
Low-Temperature Torsion - Gehman: Original										
25,000 psi, °C	-55	-53	-59	-52	-40	-34	-33	-29	-35	-22
10,000 psi, °C	-42	-48	-47	-46	-37	-31	-30	-25	-31	-19
5,000 psi, °C	-40	-44	-44	-42	-35	-28	-27	-22	-28	-18
500 psi, °C	-25	-27	-25	-25	-22	-16	-17	-11	-17	-5
Air Oven Aging, 70 h at 121°C										
Tensile, Ultimate, MPa	11.4	12.9	11.0	13.3	12.6	13.3	15.3	14.1	15.0	23.4
psi	1650	1875	1600	1925	1825	1925	2225	2050	2175	3400
Tensile Change, %	+2	+1	0	+3	-4	-10	-3	-8	+6	+6
Elongation at Break, %	420	270	350	270	290	240	270	200	280	150
Elongation Change, %	-13	-7	-13	+4	-6	-4	-7	+5	-13	+8
Hardness, Duro A, pts.	68	70	70	68	67	72	70	74	70	83
Hardness Change, pts.	+7	+7	+9	+4	+2	+3	+3	+3	+3	+2
Weight Change, %	-3.6	-4.7	-5.7	-5.5	-1.4	-1.9	-2.5	-1.4	-1.2	-1.6
180° Bend, All Pass	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Compression Set: 70 h at 121°C										
% Set	45	28	39	25	28	25	25	24	31	19

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Recipe EN03-132 Recipe Variable	1 83SS	3 DOS	4 DBES	5 CF	6 S-75	7 P-670	8 P-7068	9 P-7092	10 G-62	11 Unplas
Fuel B Immersion, 70 h at 40°C										
Tensile, Ultimate, MPa	6.2	5.9	5.9	6.0	6.2	5.7	6.4	5.3	6.2	7.8
psi	900	850	850	875	900	825	925	775	900	1125
Tensile Change, %	-45	-54	-47	-53	-53	-62	-60	-65	-56	-65
Elongation at Break, %	330	150	250	130	170	110	130	100	150	80
Elongation Change, %	-31	-48	-38	-50	-45	-56	-55	-47	-53	-43
Hardness, Duro A, pts.	30	43	33	44	40	48	44	51	41	62
Hardness Change, pts.	-31	-20	-28	-20	-25	-21	-23	-20	-26	-19
Volume Change, %	+47	+39	+43	+39	+44	+54	+45	+56	+50	+55
Weight Change, %	+25	+22	+23	+21	+24	+30	+24	+32	+27	+32
180° Bend, All Pass	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Fuel B Dry Out: 22 h at 70°C										
Hardness, Duro A, pts.	76	77	79	79	76	74	75	72	75	79
Hardness Change, pts.	+15	+14	+18	+15	+11	+5	+8	+1	+8	-2
Volume Change, %	-16	-18	-18	-18	-17	-7.7	-14	-3.4	-13	+.41
Weight Change, %	-14	-14	-15	-14	-13	-7.1	-12	-3.9	-11	-1.1
Distilled Water Immersion, 70 h at 100°C										
Tensile, Ultimate, MPa	7.2	9.3	7.2	9.8	10.2	9.3	12.1	11.5	11.0	19.,0
psi	1050	1350	1050	1425	1475	1350	1750	1675	1600	2750
Tensile Change, %	-35	-27	-34	-24	-22	-37	-24	-25	-22	-14
Elongation at Break, %	220	210	220	200	220	140	210	140	200	130
Elongation Change, %	-54	-28	-45	-23	-29	-44	-28	-26	-38	-7
Hardness, Duro A, pts.	47	54	47	52	56	48	54	51	54	72
Hardness Change, pts.	-14	-9	-14	-12	-9	-21	-13	-20	-13	-9
Volume Change, %	+78	+21	+57	+34	+32	+66	+35	+53	+32	+24
Distilled Water Dry Out: 22 h at 85°C										
Hardness, Duro A, pts.	67	69	69	68	71	73	73	75	73	85
Hardness Change, pts.	+6	+6	+8	+4	+6	+4	+6	+4	+6	+4
Volume Change, %	-2.3	+.29	-.72	+.34	+.34	+1.8	+.30	+2.2	+.02	+2.8
Weight Change, %	-1.7	-.14	-1.0	-.21	-.22	+1.4	+.08	+1.8	-.18	+2.2
Weight Change, %	+60	+17	+44	+27	+25	+51	+27	+40	+25	+18
180° Bend, All Pass	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes

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Recipe EN03-132 Recipe Variable	1 83SS	3 DOS	4 DBES	5 CF	6 S-75	7 P-670	8 P-7068	9 P-7092	10 G-62	11 Unplas
ASTM Oil #1 Immersion, 70 h at 121°C										
Tensile, Ultimate, MPa	12.9	13.8	12.4	14.1	14.1	13.5	16.7	14.1	14.7	21.4
psi	1875	2000	1800	2050	2050	1950	2425	2050	2125	3100
Tensile Change, %	+15	+8	+13	+9	+8	-9	+5	-8	+4	-3
Elongation at Break, %	370	250	330	240	280	220	270	190	270	130
Elongation Change, %	-23	-14	-18	-8	-10	-12	-7	0	-16	-7
Hardness, Duro A, pts.	69	73	73	77	73	69	72	70	68	78
Hardness Change, pts.	+8	+10	+12	+13	+8	0	+5	-1	+1	-3
Volume Change, %	-5.5	-9.8	-7.9	-10	-6.4	+2.8	-5.3	+4.8	-1.2	+5.1
Weight Change, %	-4.9	-7.3	-6.5	-7.4	-5.2	+1.4	-5.0	+2.9	-1.7	+3.1
180° Bend, All Pass	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
ASTM Oil #3 Immersion, 70 h at 121°C										
Tensile, Ultimate, MPa	8.4	9.3	7.9	9.1	9.0	9.5	10.7	9.8	9.8	14.5
psi	1225	1350	1150	1325	1300	1375	1550	1425	1425	2100
Tensile Change, %	-25	-27	-28	-29	-32	-36	-33	-36	-30	-34
Elongation at Break, %	340	210	280	160	210	160	180	140	210	110
Elongation Change, %	-29	-28	-30	-38	-32	-36	-38	-26	-34	-21
Hardness, Duro A, pts.	32	42	37	44	42	48	45	52	43	63
Hardness Change, pts.	-29	-21	-24	-20	-23	-21	-22	-19	-24	-18
Volume Change, %	+56	+45	+50	+41	+46	+49	+43	+51	+48	+48
Weight Change, %	+38	+31	+34	+29	+32	+33	+29	+34	+35	+32
180° Bend, All Pass	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes

Low-Temperature Torsion Gehman: after Air Oven Aging

25,000 psi, °C	-49	-38	-35	-45	-40	-35	-31	-29	-34	-22
10,000 psi, °C	-42	-33	-30	-32	-35	-30	-28	-24	-30	-19
5,000 psi, °C	-38	-29	-26	-27	-32	-27	-25	-21	-27	-18
500 psi, °C	-22	-9	-5	-6	-20	-16	-15	-11	-18	-1

Recipe EN03-132 Recipe Variable	1 83SS	3 DOS	4 DBES	5 CF	6 S-75	7 P-670	8 P-7068	9 P-7092	10 G-62	11 Unplas
Low-Temperature Torsion - Gehman: after Fuel B Dry Out										
50,000 psi, °C	-30	-29	-29	-28	-29	-30	-29	-30	-30	-29
25,000 psi, °C	-26	-26	-26	-25	-25	-27	-26	-28	-27	-26
10,000 psi, °C	-23	-22	-22	-22	-22	-24	-22	-24	-24	-23
5000 psi, °C	-22	-20	-21	-20	-20	-23	-21	-22	-22	-21
500 psi, °C	-4	-4	-3	-2	-1	-10	-6	-13	-6	-7
Low-Temperature Torsion - Gehman: after ASTM #1 Oil										
25,000 psi, °C	-27	-28	-28	-25	-28	-30	-28	-29	-29	-28
10,000 psi, °C	-23	-23	-23	-23	-23	-28	-23	-26	-24	-23
5,000 psi, °C	-20	-21	-21	-20	-20	-24	-20	-23	-21	-20
500 psi, °C	-6	-7	-4	-5	-7	-15	-8	-15	-9	-8
Low-Temperature Torsion - Gehman: after ASTM #3 Oil										
25,000 psi, °C	-55	-45	-48	-45	-55	-46	-45	-45	N/A	-45
10,000 psi, °C	-39	-40	-40	-40	-40	-40	-40	-39	-40	-39
5,000 psi, °C	-36	-36	-37	-37	-37	-36	-37	-36	-38	-35
500 psi, °C	-30	-30	-30	-30	-30	-30	-29	-28	-30	-27

Appendix I

Test Methods

Compounds for performance testing were mixed in a BR Banbury, except for curatives, which were added on a two-roll, 6 x 13 inch mill. Test specimens for compound performance properties were molded as follows: press temperature – 160°C (320°F), press time – 1.25 x t'c(90) min and at 833 psi on the sheet surface. Specimens for original properties, compression set, low temperature, immersions, air agings and roll spew were die cut from molded sheets .075 ± .003 inch thick.

Mooney Viscometer:	ASTM D1646-81, Monsanto Viscometer, large rotor, 1 min preheat
.	
Oscillating Disc Rheometer:	ASTM D2084-81, Monsanto Rheometer, Square Die, 3° arc, 900 cpm, 0–100 range, 30 min motor speed, 30 s preheat. MH at central point of torque rise, rate - one lb. in./5 min.
Original Properties:	
Tensile, Elongation, Modulus	ASTM D412-83, Method A, Die C
Hardness	ASTM D2240-84, ls reading
Specific Gravity	ASTM D792-66 (1979), para. 11.1
Roll Spew:	
96 h at 23 °C, 2 °C, -16 °C	HALLSTAR Method 01-79
Low-Temperature Torsion:	
Gehman	ASTM D1053
Air Oven:	ASTM D573-81
Compression Set:	ASTM D395-84, Method B, Plied Disc
Tear Resistance:	ASTM D624-81
Fluid Immersions:	ASTM D471-79
Plasticizer Analysis:	
Acid Value	AOCS Cd 3a-63
Saponification Value	AOCS Cd 3-25
Viscosity, cps (TBR)	ASTM 1824-83 (Dl545-76[1981])
Specific Gravity	ASTM D2111
Water, %	Karl Fischer

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Materials List

Material	Description	Supplier
Hypalon® 40	Chlorosulfonated Polyethylene	DuPont
Maglite® D	magnesium Oxide Powder	Hallstar
Ac 1702 Pe	Polyethylene Wax	Allied
N-774	Carbon Black	Ashland Chemical
Pe-200	Pentaerythritol	Hercules
1246 Wax	Paraffin Wax	Hallstar
Suprmix® Tac	Triallyl Cyanurate & Hydrated Amorphous Silica	Hallstar
Plasthall® 83ss	Dibutoxyethoxyethyl Sebacate Substitute	Hallstar
Plasthall® DOS	Dioctyl Sebacate	Hallstar
Plasthall® DBES	Dibutoxyethyl Sebacate	Hallstar
Plasthall® CF	Proprietary Diester	Hallstar
Monoplex® S-75	Epoxidized Glycol Dioleate	Hallstar
Plasthall® P-670	Polyester Adipate	Hallstar
Plasthall® P-7068	Low Molecular Weight Phthalate Polyester	Hallstar
Plasthall® P-7092	Polyester Glutarate	Hallstar
Paraplex® G-62	Epoxidized Soybean Oil	Hallstar
Vul-cup 40KE	Organic Peroxide	Hercules