NEW HIGH AND LOW TEMPERATURE ESTERS FOR ACRYLIC ELASTOMERS

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Acrylic elastomers are used in many demanding applications that require high heat resistance over extended periods of time. These polymers are typically plasticized at minimum levels with efficient, low-temperature esters. Normally, they do not use high levels due to the fact that these polymers have moderately low modulus values.

The standard esters used are very efficient in lowering hardness and providing low temperature, but are very volatile at the high temperature ranges in which they are exposed. This study compares two esters, TegMeR® 812 and Paraplex® A-8000, which provide improved low temperature performance after long-term high heat aging. The new esters were compared to the standard esters in two different acrylic elastomers. High and low temperature testing was conducted with the emphasis on the retention physical properties after heat aging.

INTRODUCTION

Acrylic elastomers are used for applications requiring -135°C to -150°C continuous service with intermittent exposure to -190°C. Acrylic elastomers have a saturated backbone with pendant groups attached through a carbonyl of potentially ethyl, butyl, ethylene, and oxyethyl. In addition, acrylic elastomers are polar, thus many ester plasticizers are compatible. However, because of high temperature post-cure required by most acrylics and the higher maximum temperature of application, only a few plasticizers show a reasonable degree of utility.

In this study, we focused on two new esters in two types of acrylic elastomers, Vamac G and AR HyTemp AR212HR. Polymeric esters are well known for their permanence in these elastomers, but suffer when trying to improve low temperature performance. TegMeR 812 and Paraplex A-8000 are lower molecular weight esters that have high heat resistance, but provide much needed low temperature properties after high heat aging. Also, these esters can be used in HNBR and we have some data showing similar benefits of these esters for low-temperature improvement.

EXPERIMENTAL

Formulation: **Vamac G** – 100.00, N-550–68.00*,Naugard 445 – 2.00,Stearic Acid–1.50, Armeen 18D – 0.50, Vanfre VAM – 1.00, Plasticizer as noted – 20.00
*N-550 Control Compound – 50.00

Mill Addition: Vulcofac ACT 55 – 1.80, Diak 1 – 1.50

Formulation: **HyTemp AR212HR** – 100.00, N-550 – 50.00, Stearic Acid – 1.00, Vanox CDPA – 2.00, Armeen 18D – 0.50, Vanfre VAM – 0.50, Plasticizer as noted – 10.00

Mill Addition: Rheogran XLA60 – 2.00, HMDC (Diak 1) – 0.60

Formulation: **Therban A3907**–100.0,N-990–40.00,Naugard 445–1.00,PE-AC-617–1.00 Kadox 911C – 3.00, Maglite DE – 3.00, ZMTI – 0.53, TAIC – 1.50, Plasticizer as noted – 10.00

Mill Addition: Trigonox 101-45B-PD – 8.00

TEST METHODS

Compounds for performance testing were mixed in a BR Banbury except for curatives, which were added on a two-roll mill. Test specimens for compound performance properties were molded as follows: Press Temperature – 149°C, Press Time – 1.25 x t'c(90) minutes and at 5.75 MPa on the sheet surface. Specimens for Original Properties, Low Temperature Testing, Air Oven Aging, and Immersions were die cut from molded sheets.

Mooney Viscometer	ASTM D1646-94, viscTECH+, large rotor, 1 minute preheat
Oscillating Disc Rheometer	ASTM D2084-93, RheoTECH Rheometer, round die, 3° arc, 30 sec. Preheat. MH at central point of torque rise, rate – one lb., 2.5 cm / 5 min
Original Properties	
Tensile, Elongation, Modulus	ASTM D412-92, Method A, Die C, Crosshead speed 51.0 cm/min
Hardness	ASTM D2240-91, 1s reading
Specific Gravity	ASTM D792-91
Low-Temperature	
Impact (Brittleness)	ASTM D2137-83 Method A
Gehman	ASTM D1053
Air Oven Aging	ASTM D573-81
Immersions	ASTM D471-95

Vamac

Vamac, ethylene acrylate, is used in many high-temperature applications that require good low-temperature performance, especially after heat aging. TegMeR 812 and Paraplex A-8000 provide excellent retention of low temperature properties. In this study, Vamac G was used as our base polymer. As stated, Vamac has high temperature properties up to 175°C. It also has good oil and service lubricant resistance. Since this polymer is used in many demanding applications, especially in automotive parts, retention of low temperature is important.

Four esters were evaluated along with a control compound without plasticizer:

TegMeR 812 – polyether ester

Plasthall® DBEEEG – dibutoxyethoxyethoxy ethyl adipate

TP™-759 – dibutoxyethoxyethoxy ethyl adipate

Paraplex A-8000 – polymeric ester adipate

Plasthall DBEEEG and TP-759 are chemical equivalents. They have been the standard compounding plasticizers for Vamac for many years. This type of ester has good properties in Vamac, as we will discuss in the presentation. Paraplex A-8000 is a low-molecular weight polymeric adipate ester. This ester is also an excellent choice for many Vamac applications. In this study, the esters were evaluated at 20 and 10 phr. This presentation will only discuss the 20 phr compounds.

Results

The heat history of a compound will indicate more clearly the volatility characteristics of an ester. Typically, most Vamac compounds are post-cured for 4 hours at 175°C. At this temperature and short exposure time, some volatility is measured. Table I compares weight loss of the compounds after post cure and air oven aging for 6 weeks at 150°C.

The control compound loses 1.4% of its weight. This is generally considered to be a combination of process aids and cure system volatilizing out of the compound. All of the compounds were then aged one week at 175°C, which is considered equivalent to six weeks at 150°C. The weight loss for Plasthall DBEEEG and TP-759 compounds were significant. TegMeR 812 and Paraplex A-8000 compounds have low weight losses and only slightly higher than the control compound.

If the control compound is losing 3% of its weight after post cure and heat aging, we would then expect the same weight loss in the plasticized compounds. Thus, the total plasticizer weight loss was adjusted by subtracting 3% from each compound. This result would be the better indication of ester volatility. TegMeR 812 and Paraplex A-8000 have very low weight losses as compared to TP-759 and Plasthall DBEEEG. The low volatility of these esters after heat aging is directly correlated with retention of low-temperature properties which will be discussed in the next section.

Low-Temperature Properties

Low-temperature properties were measured three different ways: glass transition by DSC, low temperature impact or brittleness, and torsion stiffness by the Gehman method. Figure 1 shows the original glass transition of each compound.

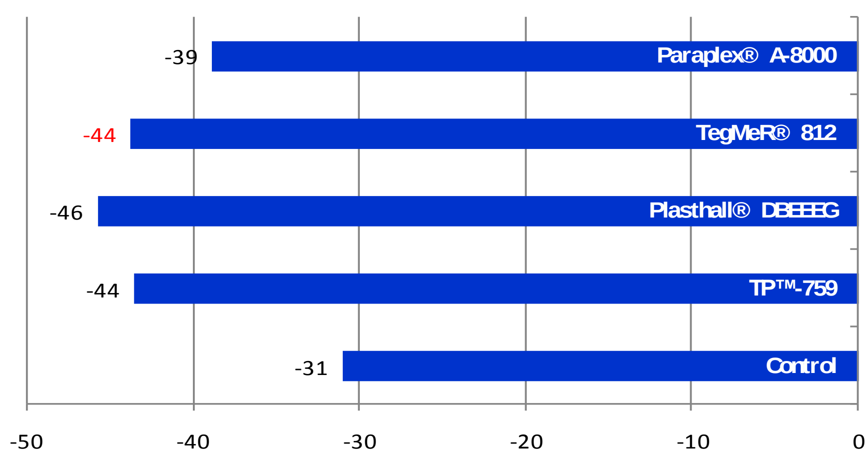

Figure 1. Original T_g, °C

All four esters lower the T_g (glass transition) of the Vamac compound substantially. As expected, the monomeric esters, TegMer 812, Plasthall DBEEEG and TP-759 provide a lower glass transition than the higher molecular weight Paraplex A-8000.

Low-temperature impact or brittleness is an old test, but a good indicator of how an ester plasticizer can influence low temperature compound. Figure 2 shows the comparison of low temperature impact for as-molded versus heat-aged compounds.

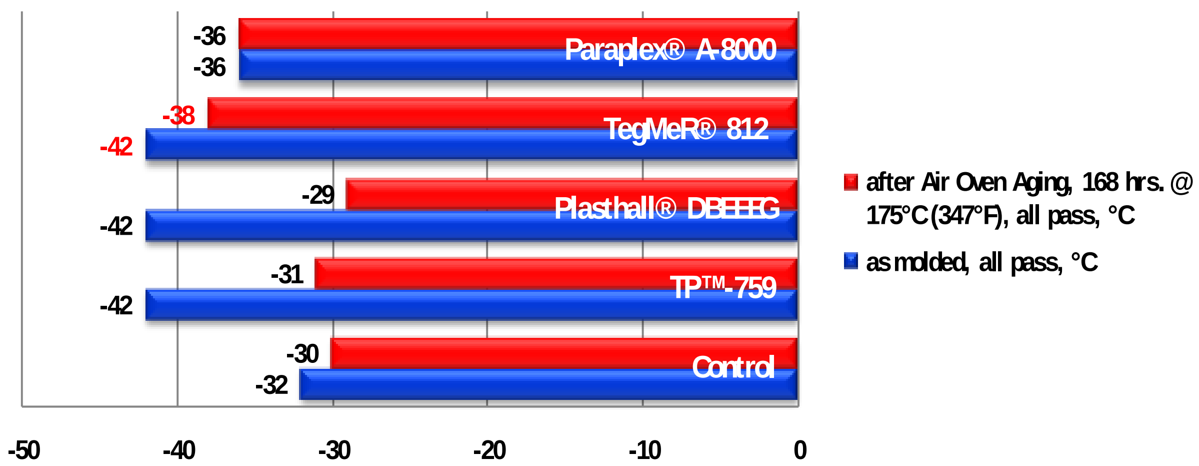

Figure 2. Low Temperature Impact, As molded vs Air Oven Aged

TegMeR 812 compound has a small change in low temperature impact after air oven aging as compared to TP-759 and Plasthall DBEEEG. Paraplex A-8000 compound shows no change in Low Temperature Impact after heat aging.

TegMeR 812, Plasthall DBEEEG and TP-759 all have equal original brittle points but, after heat aging, the differences between the compounds is significant. The TegMeR 812 compound has a small change in low temperature after air oven aging as compared to TP-759 and Plasthall DBEEEG. The results are in direct correlation to the amount of plasticizer lost during heat aging. The Paraplex A-8000 compound shows no change in low-temperature impact. It also has the lowest weight loss of the plasticized compounds after air oven aging.

T_g was also measured after heat aging to determine how the volatility of the ester can affect this property. Figure 3 compares original T_g to heat aged T_g.

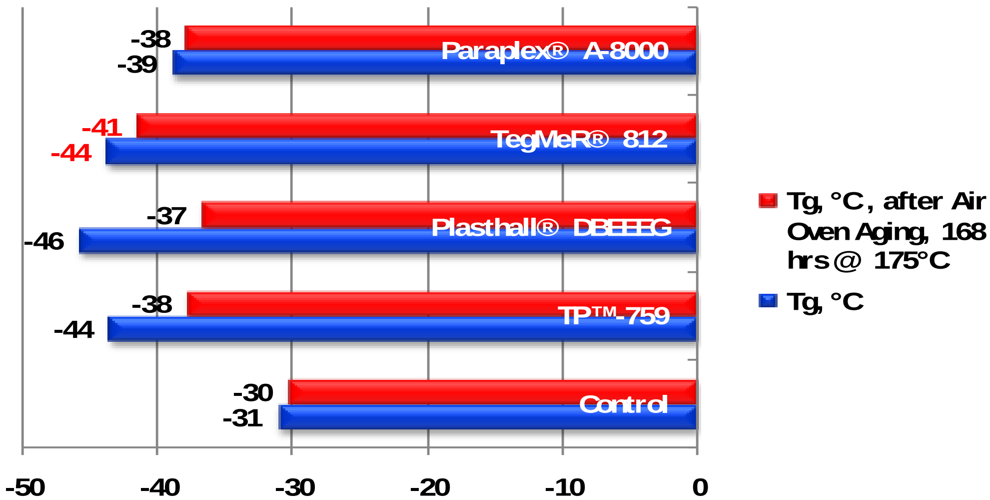

Figure 3. T_g-Original And Air Oven Aged

The Paraplex A-8000 compound and the control show the least change in T_g after heat aging. The TP-759 and Plasthall DBEEEG compounds show the greatest change. The TegMeR 812 compound has the lowest T_g after heat aging.

The Gehman results for as-molded compounds are what were expected. The heat aged results show that all compounds increased 6° to 7°C after heat aging. These results (Table II) indicate that heat aging has a major effect on the torsional stiffness of compound. Gehman results show the TegMeR 812 has the lowest value for both original and heat aged as compared to the other plasticized compounds.

Compression Set

Vamac is used in many seal applications that are under compression. Compounders know that the addition of plasticizer to Vamac causes increased compression set. Of the plasticizers tested, TegMeR 812 has the lowest compression set.

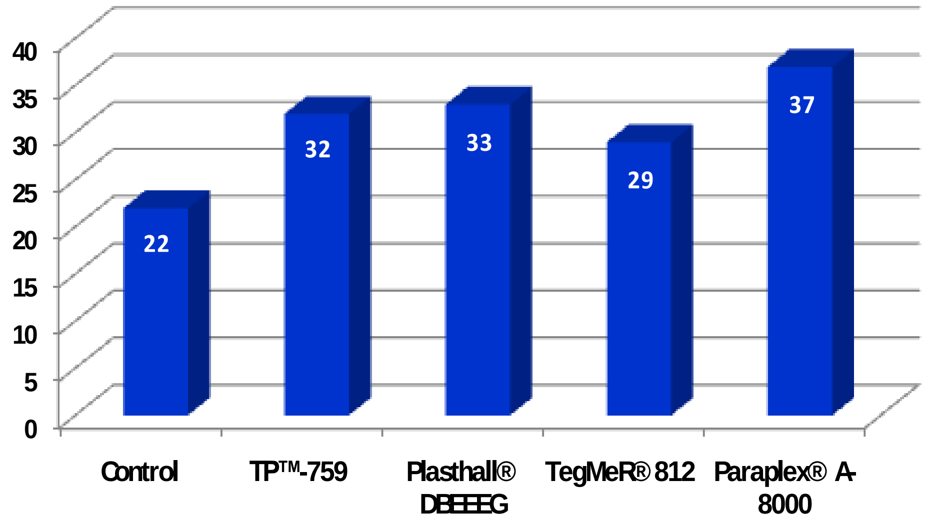

Figure 4. Compression Set, 22 hrs @ 150 °C

Automotive Service Fluids

The compounds were immersed in IRM 901 oil, IRM 903 oil, and ASTM SF105 oil for 168 hours at 150°C. The IRM 901 oil results are fairly predictable. The control compound increased in volume and weight as it absorbs the 901 oil. The three monomeric ester compounds TP-759, Plasthall DBEEEG and TegMeR 812, show weight loss and minimal volume changes. This is a common phenomenon in which a certain proportion of the monomeric ester plasticizer is extracted and replaced by the oil. This accounts for the significant difference between these three compounds and the control. Paraplex A-8000, a polymeric ester, is less extractable and allows for some oil to be absorbed into the compound.

IRM 903 oil aging shows significant volume and weight increases for all the compounds, which influences their physical properties. The TegMeR 812 compound has the lowest volume and weight change of those tested.

ASTM SF 105 oil has similar results to the IRM 903 oil. We see a large oil absorption into the compounds, especially the unplasticized control. The momomeric ester compounds show the least change in volume and weight. Service fluid data is an important piece of any compounding study, especially when comparing esters. As shown in Table III, balancing volume and weight changes are important in many applications.

HyTemp® AR 212HR - Polycrylate

Another acrylic elastomer, HyTemp AR212HR, was also evaluated in this study. We evaluated the same esters that were done in Vamac, except we added two esters, a polymeric ester, Paraplex G-50 and Plasthall TOTM. Paraplex G50 has been used in many moderate to high polarity elastomers when heat and extraction resistance to various service fluids are required. Plasthall TOTM is well known for use in many high temperature elastomers and applications. In this study, the esters were evaluated at 10phr.

Results

The heat history of a compound will indicate more clearly the volatility characteristics of an ester. Typically, most HyTemp compounds are post-cured for 4 hours at 177°C. At this temperature and short exposure time, some volatility is measured. Table IV compares weight loss of the compounds after post-cure and air oven aging for 7 days at 190°C.

Low Temperature Properties

Low temperature properties were measured by Tg (glass transition), low temperature impact or brittleness, and torsion stiffness by the Gehman method. All five esters are compared (Figure 5) and, as expected, the TegMeR 812 and Plasthall DBEEEG provide the best as-molded low temperature properties. The polymeric esters and TOTM are not quite as good because of molecular weight and bulky structures. The T_g data for the heat aged compounds show TegMeR 812 and Paraplex A-8000 to provide the lowest temperature. This data would indicate that both of these esters will provide good low temperature properties after extended heat aging.

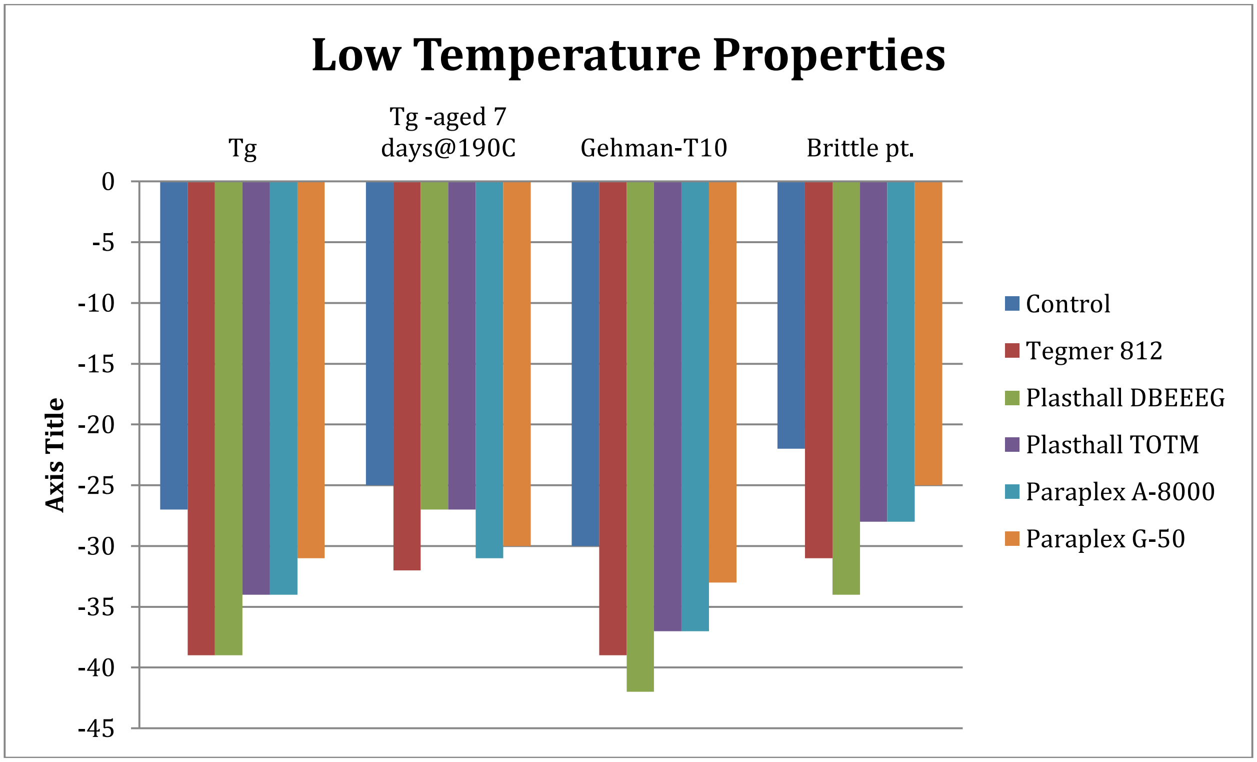

Figure 5. Tg, Gehman, Low Temperature Impact for plasticized acrylic elastomers

HNBR

HNBR is another elastomer used in many high temperature applications requiring good low temperature properties. TOTM (Tri-2-ethylhexyl trimellitate) is considered the standard ester used for HNBR, especially in high heat applications. TOTM has been known for its low volatility so it naturally has been used for plasticizing elastomers that require retention of low temperature flexibility after heat aging. In this study, TegMeR 812 and Plasthall TOTM were evaluated at 10 phr along with an unplasticized control.

The three compounds are compared for the following low temperature properties (Figure 6):

Original T_g

Air Oven Aging, 14 days @ 150°C, T_g

Gehman – T_{10}

Low Temperature Impact, Brittle Point

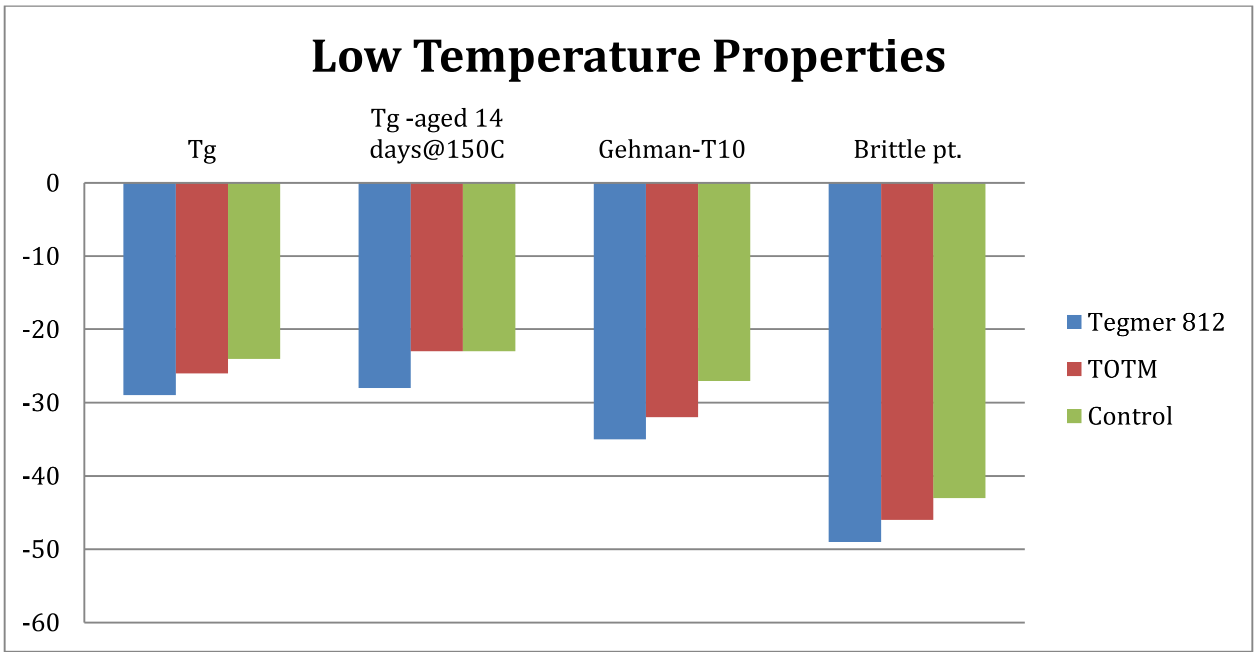

Figure 6. T_g, Gehman, Low Temperature Impact of plasticized HNBR

The compound plasticized with TegMer 812 provides better low temperature than TOTM and, because it is less volatile during heat aging, maintains low temperature properties as evidenced by T_g after heat aging.

SUMMARY

In summary, compounds made from TegMeR 812 and Paraplex A-8000 offer several advantages over other ester plasticizers in high temperature elastomers. These include lower weight loss after post cure and heat aging, and better low temperature performance. Compounds made from TegMeR 812 also have low compression set for plasticized compounds and similar volume increases after fluid aging.

ACKNOWLEGEMENT

I would like to thank John English, Kimberly Stefanisin and Nancy Gibbs of HallStar for their contributions.

Table I

Weight Loss after Post Cure and Air Oven Aging

Recipe Variable	**Control**	**TP-759**	**Plasthall DBEEEG**	**TegMeR 812**	**Paraplex A-8000**
Weight Loss,					
after Post Cure, 4 hrs. @ 175° C	-1.4	-3.1	-1.6	**-1.4**	-1.8
Air Oven, 1 wk @ 175° C	-1.6	-5.4	-6.2	**-2.5**	-1.8
Total Weight Loss, %	-3.0	-8.5	-7.8	**-3.9**	-3.6
Total plasticizer loss, %		-5.5	-4.8	**-0.9**	-0.6
% plasticizer lost		54	47	**8.8**	5.9

TegMeR 812 and Paraplex A-8000 have low weight loss after post cure and heat aging. The compounds with TP-759 and DBEEEG lose approximately 50% of plasticizer loading.

Table II

Low Temperature – Gehman

Recipe Variable	**Control**	**TP™-759**	**Plasthall® DBEEEG**	**TegMeR® 812**	**Paraplex® A-8000**
As Molded					
T_{10}, °C	-36	-41	-41	**-42**	-38
After Air Oven Aging,					
1 wk @ 175°C (347°F), All Pass					
T_{10}, °C	-29	-34	-34	**-36**	-32

Table III

Automotive Test Fluids
Change in Properties after Immersion for 168 hrs @ 150ºC

Recipe Variable	Control	TP™-759	Plasthall DBEEEG	TegMeR 812	Paraplex A-8000
IRM 901 Oil					
Tensile Change, %	-3	1	2	-2	0
Elongation Change, %	-13	-10	-7	-12	-17
Hardness Change, pts.	-7	1	3	1	-1
Volume Change, %	9.0	0.2	-0.8	-0.8	3.1
Weight Change, %	6.2	-1.2	-2.5	-1.9	1.4
IRM 903 Oil					
Tensile Change, %	-33	-34	-33	-30	-36
Elongation Change, %	-34	-39	-34	-32	-37
Hardness Change, pts.	-20	-24	-19	-22	-25
Volume Change, %	57	50	47	46	52
Weight Change, %	44	37	35	33	38
ASTM SF 105 Oil					
Tensile Change, %	-38	-29	-32	-35	-37
Elongation Change, %	-47	-39	-44	-44	-46
Hardness Change, pts.	-14	-11	-7	-10	-11
Volume Change, %	27	17	15	15	19
Weight Change, %	19	11	9.2	9.3	13

TegMeR 812 provides the lowest volume changes and weight changes for the various service fluids.

Table IV

HyTemp AR212R
Weight Loss after Post Cure and Air Oven Aging

Recipe Variable	Control	TegMeR 812	Plasthall DBEEEG	Plasthall TOTM	Paraplex A 8000	Paraplex G-50
Weight Loss,						
after Post Cure, 4 hr. @ 177° C	-1.5	-1.7	-1.8	-1.7	-1.9	-1.6
Air Oven, 1 wk @ 190° C	-3.1	-4.8	-8.3	-8.6	-3.6	-3.7
Total Weight Loss, %	-4.6	-6.5	-9.1	-10.3	-5.5	-5.3
Total plasticizer loss, %		-2.1	-4.5	-5.7	-0.9	-0.7