

“New Line of Modifiers for  
Low Polarity Elastomers and Plastics”

by

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**ABSTRACT**

This paper discusses ester-based additives to improve the properties of a number of low polarity polymers. These include elastomers like EPDM, Natural Rubber, Polychloroprene and polyolefins. Blends of thermoplastics with elastomers, thermoplastic alloys, are also targeted. These new additives have the ability to decrease low temperature properties at minimal levels. These improvements are accomplished by plasticizing the amorphous phase, while leaving the crystalline phase intact to maintain high strength.

## INTRODUCTION

Ester plasticizers have a well-known function in several thermoset elastomers and thermoplastics. The distinct advantages of using ester plasticizers are providing low-temperature or depression of  $T_g$  of the various polymers. Typically, the glass transition ( $T_g$ ) can be lowered by an ester plasticizer and still result in a strong material.

Ester plasticizers provide or modify polymers by:

- Softening the polymer
- Lower modulus
- Lower tensile strength
- Increase elongation
- Increase flexibility
- Lower glass transition
- Increase tear strength
- Increase the temperature range of usefulness
- Increase cohesion
- Modify frictional character
- Improve surface appearance
- Increase static charge

Ester plasticizers as a whole are solvents or diluents for the amorphous phases of polymers. Glassy polymers that are polar can be plasticized with esters, but careful considerations of chemical structure and solubility parameters must be exercised.

This paper will discuss the uses and function of ester plasticizers in low polarity elastomers and plastics.

## EXPERIMENTAL

The formulations used in our experimental investigations of EPDM, CR, NR and TPV compounds are as follows:

**Formulation:** Polymer as noted: 100.0, N-550 60.0, Kadox 930 5.0, Stearic Acid 1.0, Plasticizer as noted 30.0, Process oil as noted 60.0,

Mill addition: Spider sulfur 0.8, Mixland MBT 0.94, Mixland TMTD 0.63, Mixland DPTT 0.63, Mixland TDEC 0.63

**Formulation:** Neoprene WRT 100.0, Stearic Acid 2.0, Octamine 1.0, Mag Ox TN16 2.2, N-774 70.0, TMTD 0.3, Process Oil as noted 30.0, Plasticizer as noted 15.0

Mill addition: PB(ETU)75 0.8, Kadox 930 5.0

**Formulation: SMR CV 60** 100.0, Kadox 930 5.0, Stearic Acid 2.0, N-330 35.0,  
Plasticizer as noted 15.0, Process Oil as noted 30.0

**Mill Addition:** Sulfur 2.25, Santocure TBBS 0.7

**Formulation: PDC 1280** 50.0, EPDM 76/24 EP ratio 50.0, Kadox 930 1.0, SnCl<sub>2</sub> H<sub>2</sub>O (phenol  
curing agent) 0.5, Stearic Acid 1.0, SP 1056 5.0, Plasticizer and oil variable as noted 30.0

## 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 - 149C, 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, Monsanto Viscometer, large rotor, 1 minute preheat.

**Oscillating Disc Rheometer** -

ASTM D2084-93, TechPro 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

## Plasticization of Polymers

### Theory

One of the most accepted polymer plasticization theories is the free volume increase of a polymer. If the free volume of a polymer is changed at a given temperature, then its  $T_g$  will also be changed. A common method of lowering glass transition is to mix a liquid such as an ester or oil that contains more free volume than the pure polymer. The plasticizer-polymer mix will have a greater free volume than the pure polymer; thus, the plasticized polymer must be cooled to a lower temperature to reduce its free volume to the iso-free volume state that defines glass transition temperature.


### Compatibility

If plasticizer-polymer compatibility is correct, the two materials will form a homogeneous mixture during processing and once cured, the plasticizer will remain in the compound upon cooling and resting at low temperature. From a practical standpoint, it is only necessary that the compatibility be observed at a plasticizer quantity suitable to produce the desired effect. To achieve a high degree of plasticizer compatibility, it is generally necessary that the plasticizer and polymer have approximately the same polarity.

Previously, plasticizers were described as solvents of moderately high molecular weight and low volatility. Their ability to achieve and maintain compatibility with the polymer depends on the same factors that govern the behavior of simpler organic solvents and solutes. The thermodynamic basis for such interactions is expressed by Hildebrand solubility parameters, defined as the square root of cohesive energy density. Plasticizer compatibility with an amorphous polymer (or the amorphous phase of a partially crystalline polymer),  $\delta$ , normally requires values that do not differ by more than  $\pm 1.5$  (cal./cc). Solubility parameters for both polymers and plasticizers are conveniently calculated by the additive method of Small, who derived individual parameters for various atoms and groups in the molecules.<sup>1</sup> Compilations of molar attraction constants, commonly known as Small's constants, are given in many handbooks. **Table I** lists polymers and plasticizers from high to low polarity.

Table I

Polymer/PLASTICIZER Polarity Chart

<u>POLYMER</u>		<u>PLASTICIZER CLASS</u>
NYLON 6/6		AROMATIC SULFONAMIDES
NYLON 6		AROMATIC PHOSPHATE ESTERS
CELLULOSE ACETATE		ALKYL PHOSPHATE ESTERS
NBR (50% ACN)		DIALKYLETHER AROMATIC ESTERS
POLYURETHANE		POLYMERIC PLASTICIZERS
NBR 40% ACN		DIALKYLETHER DIESTERS
NITROCELLULOSE		POLYGLYCOL DIESTERS
EPOXY		
POLYCARBONATE		TRICARBOXYLIC ESTERS
ACRYLIC (PMMA)		
POLYVINYL ACETATE		POLYESTER RESINS
NBR (30% ACN)		
ACRYLATE ELASTOMERS		AROMATIC DIESTERS
POLYVINYL BUTYRAL		AROMATIC TRIESTERS (TRIMELLITATES)
EPICHLOROHYDRIN		
CHLOROSULFONATED POLYETHYLENE		
POLYVINYL CHLORIDE		ALIPHATIC DIESTERS
CELLULOSE ACETATE BUTYRATE		
POLYSTYRENE		EPOXIDIZED ESTERS
POLYCHLOROPRENE		
NBR (20% ACN)		CHLORINATED HYDROCARBONS
CHLORINATED POLYETHYLENE		AROMATIC OILS
HIGHLY SATURATED NITRILE		ALKYLETHER MONOESTERS
SBR		NAPHTHENIC OILS
POLYBUTADIENE		
NATURAL RUBBER		ALKYL MONOESTERS
HALOGENATED BUTYL		
EPDM		PARAFFINIC OILS
EPR		
BUTYL		SILICONE OILS
FLUORINATED POLYMERS		
SILICONE		

## Thermoplastic Elastomers

Olefinic thermoplastic elastomers can be subdivided into two major areas, TPO and TPV.

Thermoplastic olefins and thermoplastic elastomers are based on blends of vulcanized rubber and semi-crystalline plastics such as polypropylene, PP.

Polypropylene in its isotactic and syndiotactic forms can become very brittle at low-temperature due to their inherent crystallinity and relatively high  $T_g$ . Based on work done by Ellul of AES, it was discovered that certain “non-polar” aliphatic esters, in particular, monomeric tallates and sebacates, can effect a large depression in  $T_g$  of the polypropylene amorphous component. In this work, the plasticizer was distributed in the polypropylene and the vulcanized elastomer EPDM phases equally. <sup>2</sup>

The following ester plasticizers and paraffinic oil were then mixed with the EPDM rubber to determine physical properties and  $T_g$ .

- DOS (di-2ethylhexyl sebacate)
- Isodecyl tallate
- Butyl tallate
- Paraffinic oil--Sunpar® 150

The  $T_g$  at various volume fractions of these esters are listed in **TABLE II**.

**TABLE II**  
**EPDM/Diluent Compositions - $T_g$**

	<u>Volume Fraction</u>	<u>Calculated <math>T_g</math>, °C</u>
DOS	.52	-72
Butyl Tallate	.562	-76
Isodecyl Tallate	.562	-85
Paraffinic Oil	.562	-52

The ester plasticizers provided significantly lower  $T_g$  than the paraffinic oil.

## Plasticization of Polypropylene, Effect on $T_g$ and Comparison to EPDM

The data reported by Ellul of AES shows DOS as an excellent plasticizer for the amorphous phase of polypropylene and significant depression of  $T_g$ . Plasthall 100 and paraffinic oil were also mixed with PP and compared to DOS for  $T_g$ . **TABLE III** lists the results.

**TABLE III**

**PP/Diluent Compositions -  $T_g$**

	<u>Volume Fraction</u>	<u><math>T_g</math>, °C</u>
DOS	.40	-35
Isooctyl Tallate (P100)	.40	-35
Paraffinic Oil	.40	-12

Comparison of the tallate (P100) and sebacate ester (DOS) shows the  $T_g$  behavior to be similar.

**Effect of Various Plasticizers on  $T_g$  of Dynamically Vulcanized EPDM - Polypropylene TPEs**

The way to successful plasticization of dynamically vulcanized blends of elastomer and polypropylene was to identify plasticizers which had a low  $T_g$  and high boiling point and which were compatible over a broad temperature range with both rubber and polyolefin plastic components. The study conducted by AES evaluated various diluents ranging from mineral or synthetic oils to various types of esters on the effect on  $T_g$  of TPV based on EPDM/PP TPEs and are shown in Table IV.

TABLE IV

Effect of Plasticizer Type on  $T_g$ ,  $T_m$ , and  $X_c$  of a Dynamically Vulcanized Thermoplastic Elastomer Blend<sup>a</sup>

Plasticizer	$T_g$ , <sup>b</sup> °C		$T_m$ , °C	$X_c$ , %
	Rubber	Plastic		
NONE	-41	+10	165	45
Polyurea grease	-47	-1	159	50
Paraffinic Oil	-46	-5	158	49
Napthenic Oil (Cyclolube 213)	-48	-5	158	47
Napthenic Oil (Cyclolube 4053)	-50	-5	157	49
Napthenic Oil (Cyclolube 410)	-51	-5	158	-
Amoco 9012 polypropylene	-45	-10	159	47
Alkylalkylether diester glutarate	-55	-11	159	-
Diisocetyldodecanedioate	-56	-14	158	51
Diocetyl sebacate	-60	-18	158	53
Diocetyl azelate	-60	-22	-	-
Diisooctylnonyl adipate	-64	-24	-	-
Butoxyethyl oleate	-66	-20	158	46
n-butyl oleate	-71	-24	155	48
n-butyl tallate	-70	-24	155	45
Isooctyl tallate	-75	-26	155	51

<sup>a</sup>Dynamically vulcanized TPE,<sup>25</sup> 30 EP (D) M-70 isotactic polypropylene blend, plus 40% plasticizer phenolic resin system curative

<sup>b</sup> $T_g$ s measured from tan delta peak at 10hz.

The data clearly demonstrates that certain types of esters are extremely effective in lowering the glass transition temperatures of both EPDM and polypropylene components of the TPE. The data also indicates that only the amorphous component of the polypropylene is plasticized while the crystalline fraction remains essentially intact. This is an extremely important finding because it implies that semicrystalline polymers can be successfully plasticized with certain aliphatic esters without much detracting of elevated temperature performance.

Polymeric esters of 6000 molecular weight were found to be ineffective due to lower compatibility with EPDM and PP.



## Low-Temperature Impact Strength

One method used for measuring the strength of a compound at low temperature is Notched Izod impact. **TABLE V** lists the impact strength for several esters and paraffinic oil at -40°C in a TPV.

**TABLE V**  
**Effect of Plasticizer Type on  $T_g$ s and Impact Behavior at -40°C**  
**of a Thermoplastic Elastomer Blend<sup>a</sup>**

<b>Plasticizer</b>	<b><math>T_g</math>,<sup>b</sup> °C Rubber Phase</b>	<b><math>T_g</math>,<sup>b</sup> °C Plastic Phase</b>	<b>Notched Izod Impact at -40°C/J/m</b>
Paraffinic Oil	-59	-14	82
Diisooctyl dodecanedioate	-66	-20	124
Diisobutyl adipate	-59	-28	138
Diisooctyl adipate	-65	-29	205
Diisooctyl nonyl adipate	-64	-24	243
4-carbon linear tallate	-81	-29	414
8-carbon linear tallate	-82	-28	678
8-carbon branched tallate	-77	-29	850
10-carbon linear tallate	-79	-30	561
13-carbon linear tallate	-73	-24	687
28-carbon linear tallate	-76	-24	649

<sup>a</sup>Dynamically vulcanized TPE,<sup>25</sup> 30 EP (D) M-isotactic polypropylene (30/70), plus 32% plasticizer

<sup>b</sup> $T_g$ s measured from tan delta peak at 10hz.

### Low Polarity Polymer Modifiers

As we have seen with previous work in TPV polymers, EPDM polymers are difficult to plasticize with esters that are sufficiently compatible to avoid the plasticizer exuding (bleeding) to the surface of the elastomer upon cooling and solidification of the elastomer. Usually, hydrocarbon oils such as naphthenic oils or paraffinic oils are used to plasticize elastomers such as EPDM. While hydrocarbon-based processing oils such as paraffinic types can be used with success, the resulting plasticized compositions lack advantageous low temperature properties. Also naphthenic processing oils have a tendency to be too volatile in the more demanding applications of today. Attempts to use conventional linear dibasic acid esters, such as dioctyl adipate, dioctyl sebacate, and di-2-ethylhexyl sebacate, or phthalate esters, such as di-2-ethylhexyl phthalate, have also been unsuccessful since such conventional ester plasticizers are either incompatible with the

elastomer, resulting in exudation of the plasticizer, or are too volatile for many elastomer uses.

Even though we have proven good compatibility of tallate esters in EPDM, they are too volatile for many rubber applications.

The LPPM (Low Polarity Polymer Modifiers) were designed as high molecular weight esters with a low oxygen-to-carbon ratio with low solubility parameters and act as efficient plasticizers for elastomers such as EPDM, SBR, NR, CR and polyolefins like polypropylene. The resulting plasticized compositions have excellent low temperature properties and exhibit little or no tendency of the plasticizer to exude or bleed to the surface of the elastomer composition. Use of the LPPMs provides an advantageous balance of low temperature flexibility, impact resistance, and strength to the plasticized elastomers.

In the following examples, the LPPMs esters were mixed in several types of elastomers EPDM, natural rubber, and neoprene. The following Tables **(VI-X)** include data regarding original physical properties, processing and curing properties, compatibility, low temperature, and heat aging. In **Table VI** the EPDM polymers used were more amorphous grades and we would expect good compatibility. It should be mentioned that the LPPMs were evaluated at 30 phr and compared to a conventional paraffinic oil at 60 phr (i.e., the conventional rubber plasticizer was added to elastomer(s) at twice the amount of the rubber plasticizers).

**TABLE VI**

**Formulation:** Polymer as noted: 100.0, N-550 60.0, Kadox 930 5.0, Stearic Acid 1.0, Plasticizer as noted 30.0, Process oil as noted 60.0,

**Mill Addition:** Spider sulfur 0.8, Mixland MBT 0.94, Mixland TMTD 0.63, Mixland DPTT 0.63, Mixland TDEC 0.63

Polymer	Nordel IP 4640			Keltan 512			Buna EPT 9650			Royalene 501		
	Ethylene %	55		55			53			57		
ENB %	4.9			4.3			6.5			3.8		
Plasticizer	RX-13804	RX-13824	Sunpar 2280	RX-13804	RX-13824	Sunpar 2280	RX-13804	RX-13824	Sunpar 2280	RX-13804	RX-13824	Sunpar 2280
	<b>Mooney Viscosity at 121°C (250° F)</b>											
Minimum Viscosity	34.3	35.0	19.0	70.3	73.2	40.2	33.7	34.3	17.9	28.9	29.4	15.9
t5, minutes	5.3	4.2	7.8	3.8	3.6	4.7	5.1	4.3	8.0	5.6	5.6	8.8
t35, minutes	8.4	6.8	11.9	5.9	5.8	8.0	8.3	6.8	13.3	9.3	9.3	14.3
<b>Oscillating Disc Rheometer at 170°C ( 338°F)</b>												
ML	8.2	8.3	4.4	20.6	20.2	11.0	7.0	7.4	3.4	6.4	6.6	3.2
MH	53.1	55.7	35.5	69.9	68.2	27.8	7.2	7.5	11.9	43.8	47.1	28.6
Ts2, minutes	1.7	1.7	2.3	1.3	1.3	1.7	1.8	1.8	2.5	2.2	1.8	2.7
t'c(90), minutes	5.3	4.8	6.2	3.5	3.3	4.0	3.2	2.8	4.7	5.8	5.3	6.5
<b>Original Physical Properties</b>												
Stress @ 300 % Elong., MPa	6.3	6.7	5.8	6.3	6.8	4.8	5.5	5.6	1.9	5.4	5.6	5.0
Tensile Ultimate, MPa	12.5	12.4	11.5	15.8	16.1	15.5	15.1	16.3	14.5	14.4	14.6	13.6
Elongation @ Break, %	555	515	500	600	560	675	515	675	615	645	640	600
Hardness Duro A, pts.	60	60	52	61	61	52	51	57	48	56	57	50
<b>Low Temperature</b>												
Brittle Point, as molded, all pass °C	<-75	-72	-60	-66	-69	-57	<-75	-72	-66	<-75	<-75	-69
<b>Low Temperature Torsion – Gehman</b>												
T5, °C	-45	-44	-39	-50	-48	-44	-48	-45	-40	-50	-48	-41
T10, °C	-49	-54	-44	-57	-51	-49	-53	-52	-47	-56	-54	-48
App. Mod of Rigid Temperature, °C @	171	170	107	250	246	158	152	145	93	154	153	97
10000 psi	-59	-56	-51	-61	-59	-55	-62	-60	-56	-64	-62	-57
25000 psi	-63	-60	-59	-64	-62	-59	-66	-64	-60	-68	-66	-60

**Air Oven Aging, 70 hours @ 125°C**

Tensile Change, %	-1	-1	-16	-15	-27	-34	-26	-31	-25	-21	-14	-29
Elongation Change, %	-54	-52	-47	-59	-63	-62	-60	-64	-47	-59	-56	-58
Hardness Change, pts.	7	7	7	8	7	8	9	11	11	11	10	8
Weight Change, %	-1.5	-1.3	-1.3	-1.3	-1.2	-1.1	-1.4	-1.3	-1.3	-1.7	-1.4	-1.4

**TABLE VII**

**Formulation:** Polymer as noted: 100.0, N-550 60.0, Kadox 930 5.0, Stearic Acid 1.0, Plasticizer as noted 30.0, Process oil as noted 60.0,

**Mill addition:** Spider sulfur 0.8, Mixland MBT 0.94, Mixland TMTD 0.63, Mixland DPTT 0.63, Mixland TDEC 0.63

Polymer	RoyalEdge 4626			Vistalon 4600			Buna EPT 2450		
	Ethylene %	ENB %							
Ethylene %	64			60			59		
ENB %	6.2			4.5			4		
Plasticizer	RX-13804	RX-13824	Sunpar 2280	RX-13804	RX-13824	Sunpar 2280	RX-13804	RX-13824	Sunpar 2280
<b>Mooney Viscosity at 121°C (250° F)</b>									
Minimum Viscosity	51.2	52.1	27.0	58.6	58.1	31.1	28.9	29.5	15.6
t5, minutes	4.0	3.6	5.8	5.0	4.6	6.5	5.8	5.8	8.7
t35, minutes	6.6	5.8	10.4	7.8	7.0	10.6	9.6	9.8	14.3
<b>Oscillating Disc Rheometer at 170°C ( 338°F)</b>									
ML	13.6	14.0	7.4	15.3	15.2	8.2	6.4	6.4	3.2
MH	60.9	63.4	26.9	60.7	58.3	40.6	39.9	35.8	24.5
Ts2, minutes	1.5	1.3	2.0	1.8	1.7	2.2	2.0	2.2	2.7
t'c(90), minutes	4.7	4.3	4.3	5.8	5.3	7.3	5.7	4.8	6.2
<b>Original Physical Properties</b>									
Stress @ 300 % Elong., MPa	7.6	7.7	5.3	8.0	8.5	5.9	5.5	5.5	4.8
Tensile Ultimate, MPa	16.5	17.5	17.4	20.0	19.9	18.7	13.7	14.0	12.2
Elongation @ Break, %	490	520	660	560	535	625	655	680	600
Hardness Duro A, pts.	60	60	50	62	63	52	61	62	52
<b>Low Temperature</b>									
Brittle Point, as molded, all pass °C	-72	-72	-66	-71	<-75	-68	-72	-66	-60
<b>Low Temperature Torsion – Gehman</b>									
T5, °C	-47	-46	-43	-50	-50	-45	-36	-34	-28
T10, °C	-51	-50	-45	-55	-53	-47	-46	-44	-40
App. Mod of Rigid	171	182	160	251	244	173	221	217	138
<b>Temperature, °C @</b>									
10000 psi	-59	-57	-53	-61	-57	-56	-57	-55	-50
25000 psi	-62	-59	-60	-65	-61	-61	-65	-62	-56
<b>Air Oven Aging, 70 hours @ 125°C</b>									
Tensile Change, %	-15	-28	-29	-23	-24	-32	-7	-16	-41
Elongation Change, %	-51	-60	-59	-46	-47	-50	-56	-63	-41
Hardness Change, pts.	6	7	9	5	4	5	5	5	8
Weight Change, %	-1.3	-1.2	-1.2	-1.8	-1.7	-1.4	-1.5	-1.3	-1.3

**Results**

**Table VI** and **VII** illustrates the use of LPPMs and paraffinic oil in several EPDM elastomers of varying ethylene content. The processing and curing properties show no major differences when compared with paraffinic oils except that since the LPPMs are evaluated at lower phr they do produce higher viscosity compounds. The LPPMs provide higher tensile strength and hardness values than other plasticizers.

The low temperature properties of the compositions plasticized with the LPPMs possess better lower temperature properties than elastomers plasticized with paraffinic oil, even though the LPPMs are at 30 phr and paraffinic oil is at 60 phr. Elastomers plasticized with LPPMs exhibit an unexpected combination of high strength and hardness with excellent low temperature properties, and such properties can have importance in applications such as V-belts, radiator hoses, automotive insulation, seals and gaskets. The air oven aging results show that the dimerates are essentially equal to the paraffinic oil in weight loss.

### **Natural Rubber and Polychloroprene**

The LPPMs were mixed in Natural Rubber (SMR CV 60) and Polychloroprene (Neoprene WRT) and the data in **Tables VIII** and **IX** includes original physical properties, processing and curing, compatibility, low temperature, and heat aging. Also, the LPPMs were evaluated at 15 phr and compared to a conventional naphthenic oil at 30 phr.

**TABLE VIII**

**Formulation:** Neoprene WRT 100.0, Stearic Acid 2.0, Octamine 1.0, Mag Ox TN16 2.2, N-774 70.0, TMTD 0.3, Process Oil as noted 30.0, Plasticizer as noted 15.0

**Mill addition:** PB(ETU)75 0.8, Kadox 930 5.0

Plasticizer	<u>Process Oil</u>	
	<u>RX-13804</u>	<u>C-255-E</u>
<b><u>Mooney Viscosity at 135°C (275° F)</u></b>		
Minimum Viscosity	36.2	16.6
t5, minutes	7.3	9.5
t35, minutes	10.3	13.8
<b><u>Oscillating Disc Rheometer at 160°C ( 320°F)</u></b>		
ML	8.0	3.1
MH	50.7	19.1
Ts2, minutes	2.5	3.6
t'c(90), minutes	17.3	14.8
<b><u>Original Physical Properties</u></b>		
Stress @ 300 % Elong., MPa	---	12.3
Tensile Ultimate, MPa	15.8	13.2
Elongation @ Break, %	225	320
Hardness Duro A, pts.	69	56
<b><u>Low Temperature</u></b>		
Brittle Point, as molded, all pass °C	-40	-41
<b><u>Low Temperature Torsion – Gehman</u></b>		
T5, °C	-34	-37
T10, °C	-39	-40
App. Mod of Rigid		
Temperature, °C @		
10000 psi	-44	-45
25000 psi	-45	-48
<b><u>Air Oven Aging, 70 hours @ 125°C</u></b>		
Tensile Change, %	3	13
Elongation Change, %	-9	-48
Hardness Change, pts.	6	30
Weight Change, %	-.48	-13

**TABLE IX**

**Formulation:** SMR CV 60 100.0, Kadox 930 5.0, Stearic Acid 2.0, N-330 35.0, Plasticizer as noted 15.0, Process Oil as noted 30.0

**Mill Addition:** Sulfur 2.25, Santocure TBBS 0.7

Plasticizer	RX-13804	RX-13824	Process Oil C-255-E
<b><u>Mooney Viscosity at 168°C (335° F)</u></b>			
Minimum Viscosity	34.1	30.9	32.9
t5, minutes	1.8	2.4	3.4
t35, minutes	3.5	3.8	4.3
<b><u>Oscillating Disc Rheometer at 168°C (335°F)</u></b>			
ML	6.1	5.8	4.3
MH	6.1	5.8	4.5
Ts2, minutes	2.0	2.3	2.5
t'c(90), minutes	3.1	3.4	3.6
<b><u>Original Physical Properties</u></b>			
Stress @ 300 % Elong., MPa	4.7	5.0	3.4
Tensile Ultimate, MPa	23.6	24.2	16.3
Elongation @ Break, %	700	705	695
Hardness Duro A, pts.	46	47	40
<b><u>Low Temperature</u></b>			
Brittle Point, as molded, all pass °C	-60	-55	-55
<b><u>Low Temperature Torsion – Gehman</u></b>			
T5, °C	-57	-57	-54
T10, °C	-59	-59	-58
App. Mod of Rigid	103	118	65
Temperature, °C @			
10000 psi	-65	-64	-65
25000 psi	-68	-65	-67
<b><u>Air Oven Aging, 70 hours @ 100°C</u></b>			
Tensile Change, %	-82	-85	-73
Elongation Change, %	-61	-66	-58
Hardness Change, pts.	-6	-6	6
Weight Change, %	-13	-0.9	-0.5

### **Results**

The processing and curing properties show no major differences except that since the LPPMs are evaluated at lower phr they do produce higher viscosity



compounds. Even though the LPPMs are at 15 phr and Napthenic oil 30 phr, the LPPMs are equal in temperature properties. The combination of high strength and hardness with excellent low temperature properties are important for applications such as hoses, automotive isolators, seals and gaskets. Additionally the LPPMs are significantly lower in volatility when compared to the napthenic oil.

### **Thermoplastic Elastomer (TPV)**

The following general procedure was used in the preparation of thermoplastic elastomers. The polyolefin and rubber were placed in a heated internal mixer, with an appropriate portion of the ester and other desired additives. The mixture was heated to a temperature sufficient to melt the polyolefin component, the mixture was masticated and curative was added while mastication continued. After a maximum of mixing torque indicated that vulcanization had occurred, additional ester was added as indicated, and mixing was continued until the desired degree of vulcanization was achieved. The order of addition of the various components may vary. The compositions were then removed from the mixer, molded and tested for their physical properties.

The rubber, plastic, a phenolic curing agent and additives were blended in an electrically heated Haake mixer at a mixing speed of 77 rpm and a temperature of 120 to 190°C. Before melting of the polyolefin component, a Lewis acid was added to the blend and mixing was continued. The mixing temperature as a function of time was observed, and the onset of vulcanization was accompanied by a rapid increase in mixing torque at around 185°C. Mixing was stopped when the torque became relatively constant. The compositions were removed from the mixer and sheets were molded at 190°C and used for measurement of physical properties.

The key property for determining the efficacy of a plasticizer in improving the low temperature behavior of a thermoplastic elastomer is the glass transition temperature of both the rubber and plastic components. The glass transition temperature and heat aging characteristics of the compositions are set forth in

**Table X.**

**TABLE X**

**Glass Transition**

	<b><u>Rubber T<sub>g</sub> (°C)</u></b>	<b><u>Plastic T<sub>g</sub>(°C)</u></b>
TPV-1	-22	+8
TPV-2	-37	-16
TPV-3	-38	-17
TPV-4	-38	-17
TPV-5	-47	-22
TPV-6	-29	+2

**Air Oven Aging, 2 wks @ 125°C**

	<b>Unplas</b>	<b><u>1</u> DOS</b>	<b><u>2</u> RX13824</b>	<b><u>3</u> RX13804</b>	<b><u>4</u> RX13577</b>	<b><u>5</u> Sunpar 150</b>
Hardness Change, pts.	0	19	4	3	9	2
Weight Change, %	-0.3	-21.6	-1.5	-1.3	-12.5	-0.8

As is apparent from the above, the inclusion of LPPMs in dynamically vulcanized thermoplastic elastomer substantially reduces the  $T_g$  of both the rubber and plastic components, in comparison to the conventional processing oils. The effect of LPPMs on the heat aging of thermoplastic elastomers was studied and compared with the conventional process oil. It is apparent that the LPPMs (RX-13804 and RX-13824) have a marked improvement over a dibasic ester such as DOS and a monoester, RX-13577 (Tridecyl tallate), with significantly lower weight loss and hardness change.

### **SUMMARY**

The basic function of an ester plasticizer is to modify a polymer or resin enhancing its utility. Ester plasticizers make it possible to process elastomers easily, while also providing flexibility in the end-use product. Plasticizer-elastomer interaction are governed by many factors such as solubility parameter, molecular weight and chemical structure. Ester plasticizers provide significant improvement in low-temperature properties in various polymers that have a prominent amorphous phases. Low Polarity Polymer Modifiers (LPPMs) can plasticize semi-crystalline polymers and provide excellent low temperature properties and low volatility. By plasticizing the amorphous regions and allowing the crystalline regions to stay intact, these modifiers give low polarity polymers the strength and high temperature properties for many of the demanding applications in today's market.

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