

High Performance Ester Plasticizers For Hose Compounds

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Abstract

Traditional elastomer polymers such as nitrile, polychloroprene, chlorinated polyethylene and chlorosulfonated polyethylene have for years used moderate to low performance ester plasticizers. However, longevity requirements for rubber articles made from these elastomers have created a need for higher performance ester plasticizers. With the increasing high temperature demands required by automotive, other elastomers such as acrylic, high-saturated nitrile, epichlorohydrin and EPDM are replacing the more traditional elastomers.

Plasticizers commonly used for the traditional, as well as the high temperature polymers are extractable, incompatible, or too volatile. This paper provides information on plasticizers that are designed for traditional elastomers and high performance polymers. The test data will include heat aging, extraction by hydrocarbons, and low-temperature as molded after aging. The information provided indicates that permanence of the plasticizer after these various agings is the key to retention of physical properties.

Introduction

End uses for elastomer compounds are quite diverse, but they can be loosely categorized as being either general performance or higher performance applications. Each of these performance categories requires a different set of considerations in terms of compounding with ester plasticizers. An ester plasticizer, in its simplest concept, is a high-boiling organic solvent which when added to an elastomeric polymer reduces stiffness and permits easier processing. For general performance applications, compounders require moderate performance in several areas without particular emphasis on any one. Some general performance ester plasticizers used in the marketplace today are DOA, DIDA, DIDP, DOP, DINP and other phthalates and adipates made from straight-chain alcohols of seven to eleven carbons in length.

Ester plasticizers are commonly used only for their as-molded low temperature contribution. Ester plasticizers used for high performance applications must have excellent non-volatility upon heat aging and extraction resistance to various fluids. Measuring retention of low temperature properties after aging is an indicator of plasticizer permanence.

In this paper, several elastomers are evaluated to show how choosing the appropriate monomeric or polymeric ester plasticizer can enhance performance and longevity of rubber parts.



Discussion

Ester plasticizers discussed in this paper will be both monomeric and polymeric.

Polymeric Plasticizers - Polymeric polyester plasticizers may be used in higher performance applications where superior plasticizer non-volatility, fluid chemical extraction resistance are critical.

Polymeric plasticizers are produced by reacting a dibasic carboxylic acid with a glycol or a mixture of different dibasic glycols. When the molecules are reacted, the chain propagation or building may be terminated by the use of monofunctional carboxylic acids or alcohols. Some polymeric plasticizers are also produced using no terminator.

Following is a representation (Fig. 1) of the production of an acid, alcohol and a non-terminated polymeric polyester, which assumes that stoichiometrically correct quantities of dibasic carboxylic acid, glycol, and mono functional carboxylic acid or alcohol have been reacted together to yield a polymeric plasticizer of a viscosity (or molecular weight) within a given range.



Fig. 1. Polyester plasticizer structures

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Polymeric ester plasticizers can also be terminated with alcohols or nonterminated. Polymeric plasticizers have many advantages when compared to monomeric plasticizers. Table I compares monomeric and polymeric ester plasticizers on performance trends.

TABLE I

<u>Property</u>	Monomeric Trend	Polymeric Trend
Processing Ease	Good to Excellent	Poor to Excellent
Compatibility	Dependent on Chemical Structure	Dependent on Chemical Structure
Softening Efficiency	Good to Excellent	Poor to Fair
Low-Temperature Flexibility Extraction Resistance	Good to Excellent	Poor to Fair
Organic	Fair to Excellent	Poor to Good
Volatility	Poor to Good	Good to Excellent

Polymeric Esters Permanence - The permanence of a polymeric plasticizer in an elastomer compound depends upon three major factors, which include structure, molecular weight/viscosity and polarity. Polymerics composed of branched structures are more permanent, especially in applications requiring migration and extraction resistance. Branching tends to hinder movement or entangle the plasticizer with the polymer matrix. Although linear structures are more migratory, they do yield better low temperature properties and are less volatile. Higher molecular weight polymeric esters provide greater permanence. These large molecules have less mobility, thus, more difficult to be removed.

Polymeric esters must be selected carefully when considering the varying solubility parameters of elastomers. Polymeric esters typically are polar materials and find good compatibility in polar elastomers, such as nitrile. Polymeric esters that are marginally compatible are less permanent, which can lead to increased migration, higher volatility and more extraction.

Paraplex Approach - The Paraplex Approach is foremost a molecular design system for ester plasticizers. The system is driven by our customers' performance requirements. The data that has been collected in our laboratory for over 50 years has been inputted into a computer program. This data includes all the chemical structures of the esters we synthesize as well as their compound physical properties. This system allows for rapidly adjusting raw materials and molecular weight to precise compound requirements.

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Fig. 2 is a typical surface response map that is generated by our program. One of the most important features of this program is that the surface response map can show how the composition can be, in one case, the optimal product (arrow illustrated in Fig. 2) or, if the raw material composition were changed slightly, the performance would drastically change. Following are the standard compound physical properties used to generate the surface response maps. Physical properties not listed can be included which generate the product composition.

Performance Properties

Viscosity and Curing Properties

Original Properties 100% Elongation Tensile Ultimate Elongation at Break Hardness Duro A Brittle Point Low Temp. Torsion Surface Energy

Air Oven Aging 100% Stress Change Tensile Ultimate Change Elongation Change Hardness Change Weight Change 24 h Soapy Water

Migration Resistance ABS Polystyrene Extractions 24 h. Humidity 9 d Humidity Hexane Cottonseed Oil DI Water 7 Day Soapy Water ASTM Oil #1 IRM 903 ASTM Fuel C



Polymeric Ester - High Performance Applications - Polymeric esters are used in many high performance applications that require a combination of low volatility and extraction resistance to various fluids. General purpose monomeric esters typically cannot hold up to severe service conditions. Rubber compounds in underhood automotive applications must retain their effective use over a long period of time. Polymeric esters are especially suited for high performance elastomers such as nitrile, high saturated nitrile and polyacrylates. Polymeric esters also have found utility in chlorinated polyethylene, chlorosulfonated polyethylene and fluoroelastomers.

HNBR - One example of how polymeric esters can enhance a high performance elastomer is depicted in Fig. 3. High-saturated nitrile is used in many high heat applications. The use of 8-10 trimellitate is well documented as the plasticizer of choice for HNBR. As the graph depicts, a phthalate/adipate polymeric ester with a molecular weight of 1000 will enhance long-term heat aging properties.



Fig. 3. - Heat resistance of plasticized HNBR compounds

Many plasticizers have been evaluated in HNBR for compatibility. The high degree of saturation and potential crystalline character severely limit the choice of plasticizers. After several screening evaluations, a plasticizer that did show some compatibility advantages was a polyester glutarate (G-24,000). This plasticizer has a molecular weight of 5,000. The G-24,000 and 8-10 TM-E were compared in a standard HNBR recipe at 20 PPHR. (Table II).

The G-24,000 and 8-10 TM-E were found to provide comparable performance with regard to Mooney Viscosity reduction at 150°C, compatibility and have equal weight losses after 70 hours at 150°C. The G-24,000 was less extractable in Fuel C, ASTM #1 and #3 Oils. The compound with 8-10 TM-E has improved low



temperature properties and permanence following distilled water immersion dry out.

Flasticizer companson in mudit at 20 FFTIK				
<u>Plasticizer</u>	<u>None</u>	<u>8-10 TM-E</u>	Polyester Glutarate <u>(G-24,000)</u>	
Mooney Viscosity at 150°C	83.0	39.5	48.5	
Duro A, Hardness	79	69	73	
Gehman Torsion, °C at 10,000 psi	-27	-35	-31	
Air Oven, 7 d at 150°C, % weight change	-2.4	-2.6	-2.4	
ASTM Fuel C Immersion, 70 h at 40°C, % weight change, dryout	-1.5	-11	-4.8	
ASTM #1 Oil Immersion, 70 h at 150°C, % weight change	41	-11	-1.2	
Distilled Water Immersion, 70 h at 100°C % weight change	+ 3.0	+ 3.6	+ 9.9	

TABLE IIPlasticizer Comparison in HNBR at 20 PPHR

The results for Fuel C and ASTM #1 Oil show that 8-10 TM-E is totally extracted from the compound. The G-24,000 is much less extractable in these hydrocarbon mediums.

Acrylics - Acrylic elastomers are used for applications requiring 149-177°C continuous service with intermittent exposure to 204°C.

Acrylic elastomers have a saturated backbone with pendant groups attached through a carbonyl of such things as ethyl, butyl, ethylene and oxyethyl. In addition, acrylic elastomers are similar to nitrile in their polarity. A large variety of plasticizers are compatible with acrylics. However, because of a high temperature post cure required by some acrylics and the higher maximum temperature of application, only a few plasticizers show a reasonable degree of utility. Another property of acrylics that limits the amount of plasticizer



incorporated is tensile strength. Acrylics generally do not have and are not used in applications requiring high tensile strength. Many compounders try to use the least amount of plasticizer to achieve their end requirements.

Polymeric plasticizers that are efficient in lowering hardness, providing good low temperature properties, and have low volatility in both post-cure and heat aging are ideal candidates for acrylics. Two polymeric plasticizers that meet these requirements are polyester adipates with a molecular weight of 1000. A study of A-1000A, A-1000B and Dibutoxyethoxyethyoxyethyl glutarate (DBEEEG) in Vamac D for original and aged physical properties indicates some major benefits of using polymeric esters. Table III highlights data from this study conducted by DuPont Dow Elastomers L.L.C. DBEEEG, a high molecular weight glycol ether ester monomeric plasticizer, is commonly recommended for acrylic elastomers. In this study, A-1000A and A-1000B show they are equal or better than DBEEEG softening efficiency and original low temperature. A-1000A and A-1000B provide better permanence after heat aging, resulting in the retention of physical properties.

The compound containing A-1000B shows advantages in compression set and retention of low-temperature properties. It is important to note the original tensile strengths of each compound. As was stated earlier, acrylic elastomers have low tensile strength without plasticizer. The addition of plasticizer will decrease tensile strength. The A-1000A and A-1000B compounds have original tensile strengths of 11.2 MPa and 11.3 MPa, respectively, which is a marked difference from the DBEEEG (8.8 MPa) compound.

Plasticizer Variable	A-1000A	A-1000B	DBEEEG
Original-Post cured 2 h at 175°C			
Tensile Strength, MPa	11.2	11.3	8.8
Hardness, Shore A, Pts.	72	69	71
Aged 1008 h. at 150°C			
% Elongation Change	-14.6	-21.6	-25.9
Hardness, Shore A (pts change)	11	13	17
% weight loss	3.75	3.85	7.13
Low Temperature Testing			
DSC, Inflection, °C, original	-31.9	-33.8	-36.8
After 1008 h. at 150°C	-28.4	-30.1	-28.1
Gehman, T-10,°C	-21.9	-25.4	-25

TABLE III Plasticizer Evaluation in Vamac D at 10 PPHR

Compression Set, Method B, Dried Pellets 70 Hrs at 150°C - Post cured (Cooled 2 h in Clamps)	41	37	48
ТА	ABLE IV		
Plasticizer Variable	<u>A-1000-A</u>	<u>A-1000B</u>	DBEEEG
Transmission Fluid Immersion, 1000 h at 150°C (302°F).			
Hardness, Duro A, pts.	54	53	58
Hardness Change, pts.	-2	-3	+5
Weight Change, %	+12	+14	+13
Volume change, %	+18	+20	+18

180° Bend, all pass

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CPE - Chlorinated polyethylene (CPE) was developed for use in applications involving serviceability where oil resistance, ozone and weathering resistance are important. CPE's can generally be used in applications that encounter service temperatures up to 149°C. This polymer owes its ozone and weathering resistance, and relatively good heat aging properties to the fact that it has a saturated backbone. Also, the presence of chlorine in the elastomer imports enhanced oil resistance.

Yes

Yes

Yes

Common plasticizers for CPE are high oxirane content epoxidized soybean oil, and TOTM (tri-octyl trimellitate). These plasticizers provide a good overall balance of heat and oil resistance that is needed for applications up to 150°C. Polymeric plasticizers have not been used to a great extent because of observed porosity in cured compounds.

The porosity problem has not been investigated thoroughly, but is believed to be related to the chlorine content and cure systems breaking down the polymeric esters. In our evaluations of polymeric esters, one plasticizer did provide the necessary permanence properties needed for CPE, without causing porosity in cured compound. The polymeric adipate, A-1000A can be used in all cure systems for CPE without a problem.

A comparison of physical properties for A-1000A, ESO and TOTM in CPE is provided in Table V. The adipate-based polyester, A-1000A, provided a number of interesting properties relative to TOTM and ESO.

- Greater Mooney viscosity reduction
- Lower percent change of elongation, hardness and weight after an aging for 70 hours at 150°C



- Lower change of hardness, volume and weight after Fuel C immersion
- Significantly lower change after immersion in ASTM 2 oil for 70 hours at 150°C

TABLE V

Plasticizers for CPE at 35 PPHR

Plasticizer Variable	ESO	A-1000A	TOTM
wolecular weight	1000	1000	550
Low-Temperature			
D-2137, °C	-35	-34	-42
D-1053, °C.	72	69	71
Air Oven, 70 h at 150°C			
% Elongation Change	-20	-6	-30
% Weight Change	-1.8	-2.6	-3.9
ASTM 2 Oil, 70 h at 150°C			
% Elongation Change	-20	-9	-32
% Weight Change	+41	+38	+43

NBR - Nitrile rubber is typically used in applications up to 125°C. The majority of nitrile compounds are plasticized with monomeric esters. The oil and fuel applications for NBR generally require that the plasticizer be extracted to some extent to meet volume swell requirements. There are many applications that require more permanence especially to heat and hydrocarbon extraction. Basically, all polymeric esters have good compatibility in NBR. The compatibility of ester plasticizers can vary depending upon the ACN content of the nitrile and the amount used. The higher ACN content nitriles require higher polarity esters and the lower ACN content nitriles require esters of lower polarity. Since the majority of the polymeric esters can be used in nitrile, we will only highlight a few products that have some high performance properties.

A-1000A	(Polyester Adipate) - Good combination of low-temperature,
	efficiency, property retention after oil aging, fuel hoses
G-24,000	(Polyester Glutarate) - High temperature and oil resistance
	hydrocarbon solvent resistance, print roll compounders
A-150,000	(Polyester Adipate) - High temperature and oil resistance oil
	seals
S-160,000	(Polyester Sebacate) - High temperature and oil resistance,
	hydrocarbon solvent resistance, oil field wire and cable

Olefinic and EPDM - 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 Tg. 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 Tg of the polypropylene amorphous component. In this work, the plasticizer was distributed in the polypropylene and the vulcanized elastomer EPDM phases equally.

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

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

The Tg at various volume fractions of these esters is listed in Table VI.

TABLE VI EPDM/Diluent Compositions -Tg

	Volume	Calculated
	Fraction	Tg, °C
DOS	.52	-72
Butyl Tallate	.562	-76
Isodecyl Tallate	.562	-85
Paraffinic Oil	.562	-52

The ester plasticizers provided significantly lower Tg than the paraffinic oil.

Plasticization of Polypropylene, Effect on Tg 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 Tg. Plasthall[®] 100 and paraffinic oil were also mixed with PP and compared to DOS for Tg. Table VII lists the results.



TABLE VII PP/Diluent Compositions - Tg

	Volume Fraction	Tg, °C
DOS	.40	-35
Isodecyl Tallate (P100)	.40	-35
Paraffinic Oil	.40	-12

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

Effect of Various Plasticizers on Tg 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 Tg 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 Tg of TPV based on EPDM/PP TPEs and are shown in Table VIII.

TABLE VIII

Effect of Plasticizer Type on Tg, Tm, and Xc of a Dynamically Vulcanized Thermoplastic Elastomer Blends

TPE	Plasticizer	Tg,b °C Rubber	Tg,b °C Plastic	Tm, °C	Xc, %
TIA	None	-41	+10	165	45
TIB	Polyurea grease	-47	-1	159	50
TIC	Paraffinic Oil	-46	-5	158	49
TID	Napthenic Oil (Cyclolube 213)	-48	-5	158	47
TIE	Napthenic Oil (Cyclolube 4053)	-50	-5	157	
TIF	Napthenic Oil (Cyclolube 410)	-51	-5	158	49
TIG	Amoco 9012 polypropylene	-45	-10	159	47
TIH	Alkylalkylether diester glutarate	-55	-11	159	-
TII	Diisoctyldodecanedioate	-56	-14	158	51
TIJ	Dioctyl sebacate	-60	-18	158	53

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TIK	Dioctyl azelate	-60	-22	-	-
TIL	Diisooctylnonyl adipate	-64	-24	-	-
TIM	Butoxyethyl oleate	-66	-20	158	46
TIN	n-butyl oleate	-71	-24	155	48
TIO	n-butyl tallate	-70	-24	155	45
TIP	Isooctyl tallate	-75	-26	155	51

a Dynamically vulcanized TPE, 30 EP (D) M-70 isotactic polypropylene blend, plus 40 percent plasticizer phenolic resin system curative.
b Tg'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 detraction 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 IX lists the impact strength for several esters and paraffinic oil at -40°C in a TPV.

TABLE IX

Effect of Plasticizer Type on Tgs and Impact Behavior at -40°C of a Thermoplastic Elastomer Blends

		Tg, ^b °C	Tg, ^b °C	Notched Izod Impact
TPE	Plasticizer	Rubber Phase	Plastic Phase	at -40°C/J/m
T2A	Paraffinic Oil	-59	-14	82
T2B	Diisooctyldodecanedioate	-66	-20	124
T2C	Diisobutyl adipate	-59	-28	138
T2D	Diisooctyl adipate	-65	-29	205
T2E	Diisooctylnonyl adipate	-64	-24	243
T2F	4-carbon linear tallate	-81	-29	414
T2G	8-carbon linear tallate	-82	-28	678

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T2H	8-carbon branched tallate	-77	-29	850
T2I	10-carbon linear tallate	-79	-30	561
T2J	13-carbon linear tallate	-73	-24	687
TIK	28-carbon linear tallate	-76	-24	649

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

b Tg'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 napthenic processing oils have a tendency to be to 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-2ethylhexyl 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 to 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 an 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 (X-XIV) include data regarding original physical properties, processing and curing properties, compatibility, low temperature, and heat aging. In Table X 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 X

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

Ethylene % ENB %	55 4.9		55 4.3			53 6.5			57 3.8			
Plasticizer	RX- 1380 4	RX- 1382 4	Sunpa r 2280	RX- 13804	RX- 1382 4	Sunpa r 2280	RX- 1380 4	RX- 1382 4	Sunpa r 2280	RX- 13804	RX- 1382 4	Sunpa r 2280
Mooney Viscosity at	t 121°C											
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
Oscillating Disc Rhe	eometei	r at 170	°C									
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
ťc(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
Original Physical Pr	opertie	S										
Stress at 300 %	6.3	6.7	5.8	6.3	6.8	4.8	5.5	5.6	1.9	5.4	5.6	5.0
Elong., MPa												
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 at 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
Low Temperature Brittle Point, as molded, all pass °C	<-75	-72	-60	-66	-69	-57	<-75	-72	-66	<-75	<-75	-69



Polymer Ethylene %	No	ordel IP 4640 55		Keltan 512 55		Buna EPT 9650 53			Royalene 501 57			
EIND 70		4.9			4.3			0.0			3.0	
Plasticizer	RX- 1380	RX- 13824	Sunpa r 2280	RX- 13804	RX- 13824	Sunpa r 2280	RX- 13804	RX- 1382	Sunpa r 2280	RX- 13804	RX- 13824	Sunpa r 2280
	4		Low	Temper	ature To	rsion – G	ehman	4				
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	171	170	107	250	246	158	152	145	93	154	153	97
Temperature, °C at												
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 A	ging, 70 l	hours at 1	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

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TABLE XI

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	RoyalEd	dge 4626	5	Vistalon	4600		<u>Buna EP</u>	<u>'T 2450</u>	
Ethylene %	64			60			59		
ENB %	6.2			4.5			4		
Plasticizer	RX- 13804	RX- 13824	Sunpa r 2280	RX- 13804	RX- 13824	Sunpa r 2280	RX- 13804	RX- 13824	Sunpa
Mooney Viscosity at 121°C	(250° F)	10024	1 2200	10004	10024	1 2200	10004	10024	1 2200
Minimum Viscositv	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
Oscillating Disc Rheometer	at 170°C	C (338°F	5)						
ML	13.6	14.0	, 7.4	15.3	15.2	8.2	6.4	6.4	3.2
МН	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
ťc(90), minutes	4.7	4.3	4.3	5.8	5.3	7.3	5.7	4.8	6.2
Original Physical Properties	;								
Stress at 300 % Elong.	7.6	7.7	5.3	8.0	8.5	5.9	5.5	5.5	4.8
MPa									
Tensile Ultimate, MPa	16.5	17.5	17.4	20.0	19.9	18.7	13.7	14.0	12.2
Elongation at Break, %	490	520	660	560	535	625	655	680	600
Hardness Duro A, pts.	60	60	50	62	63	52	61	62	52
Low Temperature									
Brittle Point, as molded, all	-72	-72	-66	-71	<-75	-68	-72	-66	-60
pass °C									
Low Temperature Torsion -	Gehma	n							
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
Temperature, °C at									
10000 psi	-59	-57	-53	-61	-57	-56	-57	-55	-50
25000 psi	-62	-59	-60	-65	-61	-61	-65	-62	-56
Air Oven Aging, 70 h at 125°	°C								
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 X and XI 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 XII and XIII 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 XII

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

		Process
Plasticizer	RX-	Oil
	<u>13804</u>	<u>C-255-E</u>
Mooney Viscosity at 135°C (275° F)		
Minimum Viscosity	36.2	16.6
t5, minutes	7.3	9.5
t35, minutes	10.3	13.8
Oscillating Disc Rheometer at 160°C		
<u>(320°F)</u>		
ML	8.0	3.1
MH	50.7	19.1
Ts2, minutes	2.5	3.6
ťc(90), minutes	17.3	14.8
Original Physical Properties		
Stress at 300 % Elong., MPa		12.3

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15.8 225 69	13.2 320 56
-40	-41
-34	-37
-39	-40
-44	-45
-45	-48
3	13
-9	-48
6	30
48	-13
	15.8 225 69 -40 -34 -39 -44 -45 3 -9 6 48

TABLE XII

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

			Process Oil
Plasticizer	<u>RX-13804</u>	RX-13824	C-255-E
Mooney Viscosity at 168°C (335°F)			
Minimum Viscosity	34.1	30.9	32.9
t5, minutes	1.8	2.4	3.4
t35, minutes	3.5	3.8	4.3
Oscillating Disc Rheometer at			
<u>168°C (335°F)</u>			
ML	6.1	5.8	4.3
MH	6.1	5.8	4.5
Ts2, minutes	2.0	2.3	2.5
ťc(90), minutes	3.1	3.4	3.6
Original Physical Properties			
Stress at 300 % Elong., MPa	4.7	5.0	3.4
Tensile Ultimate, MPa	23.6	24.2	16.3
Elongation at Break, %	700	705	695
Hardness Duro A, pts.	46	47	40
Low Temperature			



Brittle Point, as molded, all pass °C Low Temperature Torsion –	-60	-55	-55
Gehman			
T5, °C	-57	-57	-54
T10, °C	-59	-59	-58
App. Mod of Rigid	103	118	65
Temperature, °C at			
10000 psi	-65	-64	-65
25000 psi	-68	-65	-67
Air-Oven Aging, 70 h at 100°C			
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 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.

Thermplastic 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 XIV.

TABLE XIV

	Rubber Tg (°C)	Plastic Tg (°C)
TPV-1	-22	+8
TPV-2	-37	-16
TPV-3	-38	-17
TPV-4	-38	-17
TPV-5	-47	-22
TPV-6	-29	+2

Glass Transition

Air Oven Aging, 2 w at 125°C

	Unplas	DOS	RX- 13824	RX- 13804	RX- 13577	Sunpar 2280
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 Tg 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 prominent amorphous phases. Low Polarity Polymer Modifiers (LPPMs) can plasticize semicrystalline 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.

References

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