HALLSTAR

New Developments in Ester Technology

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Abstract

This paper will discuss three areas of new ester development. These include the Paraplex Approach, a computer modeling program, low polarity esters and HallGreen® esters, a new line of renewable and sustainable esters for rubber and thermoplastics.

The Paraplex Approach is a molecular design system that Hallstar has developed to characterize and synthesize solutions to the very tightly defined performance requirements of our customers. By using our existing performance data, application knowledge and the latest in computer technology, we are capable of very rapidly adjusting raw materials in precise combinations to meet specifications. Customers specify targets for plasticizer performance properties and prioritize the critical measures of utility, which are most significant to the end application. Performance properties include all typical plasticizer criteria, such as general physical properties, air oven aging, extractions, immersions and migration resistance.

Ester-based additives improve the properties of a number of low-polarity polymers. These include polypropylene, elastomers like ethylene propylene diene monomer (EPDM), natural rubber and styrene/ ethylene/ butadiene polymers. Blends of thermoplastics with elastomers, or 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.

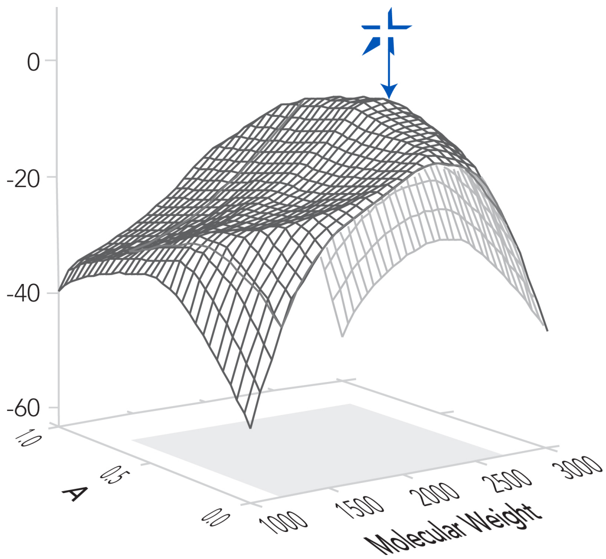
HallGreen® esters are new innovative esters that are plant-derived and perform as well as traditional esters derived from petroleum-based products. HallGreen® esters are designed to be used in a variety of products—from medical devices to children's toys and from flooring to water service—anywhere a manufacturer wants to reduce or eliminate esters that are reportable or considered hazardous to the environment.

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 and their compound physical properties. This system allows for rapidly adjusting raw materials and molecular weight to precise compound requirements. Figure 1 is a typical surface response map 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. 1), 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.

Fig. 1



Performance Properties

Viscosity and Curing Properties

<u>Original Properties</u>
- 100% Elongation
- Tensile Ultimate
- Elongation W Break
- Hardness Duro A
- Brittle Point
- Low Temp. Torsion
- Surface Energy

<u>Air Oven Aging</u>
- 100% Stress Change
- Tensile Ultimate Change
    - Elongation Change
    - Hardness Change
    - Weight Change

<u>Migration Resistance</u>
- ABS
- Polystyrene

<u>Extractions</u>
-24 h Humidity
-9 d Humidity
-Hexane
-Cottonseed Oil
-DI Water
-24 h Soapy Water
-7 d Soapy Water
-ASTM Oil # 1
-IRM 903
-ASTM Fuel C

Low-Polarity Polymer Modifiers

The low-polarity polymer modifiers (LPPM) 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, styrene-butadiene rubber (SBR), natural rubber (NR) and chloroprene rubber (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. The use of 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 EPDM and santopreme thermoplastic vulcanizates (TPV). The following table includes data regarding original physical properties, processing and curing properties, compatibility, low temperature and heat aging. 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).

Formulation: Polymer as noted: 100.0, N-550 60.0, Kadox 930 5.0, Stearic Acid 1.0

Mill addition: Plasticizer as noted 30.0, Process oil as noted 60.0, 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 %	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**
<u>Mooney Viscosity</u> at 121°C									
Minimum Viscosity	51.2	52.1	27.0	58.6	58.1	31.1	28.9	29.5	15.6
<u>Oscillating Disc Rheometer</u> at 170°C									
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
<u>Original Physical Properties</u>									
Stress at 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 at Break, %	490	520	660	560	535	625	655	680	600
Hardness Duro A, pts.	60	60	50	62	63	52	61	62	52
<u>Low Temperature</u>									
Brittle Point, as molded, all pass °C	-72	-72	-66	-71	<-75	-68	-72	-66	-60

Low-Temperature Torsion – Gehman									
T10, °C	-51	-50	-45	-55	-53	-47	-46	-44	-40
Air Oven Aging, 70 h at 125°C									
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

The table 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 because the LPPMs are evaluated at lower PHR they 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 be important 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.

Thermoplastic Elastomers

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 the following table.

Glass Transition

	Rubber T_g (°C)	Plastic T_g (°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

Air Oven Aging, 2 weeks at 125°C

	1 Unplas	2 DOS	3 RX13824	4 RX13804	5 RX13577	6 Sunpar 150
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) are 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.

HallGreen® esters

HallGreen® esters are new innovative esters that are plant-derived and perform as well as traditional esters derived from petroleum-based products. HallGreen® esters are designed to be used in a variety of products—from medical devices to children's toys and from flooring to water service—anywhere a manufacturer wants to reduce or eliminate esters that are reportable or considered hazardous to the environment. Following are examples of the various green ester chemicals available.

Dicapryl Sebacate
Dicaprylic/Capric Sebacate
Capryl Tallate
Dicapryl Lactate Adipate
Capryl Lactyl Tallate
Dicapryl Dimerate
Dicaprylic/Capric Dimerate
Dicapryl Lactate Sebacate
Dicapryl Lactate Adipate

Performance Properties

HallGreen® RX-14010		Acetylated Citrate Ester	
PPHR	7	PPHR	67
Shore A Hard.	67	Shore A Hard.	66
Low Temp, Brittle Pt, C	-37	Low Temp, Brittle Pt, C	-30
Ten. Strength, psi	2240	Ten. Strength, psi	2355
Ultimate Elong., %	395	Ultimate Elong., %	390
Air Oven Aging, 70 h at 121°C			
Weight change, %	-9.9	Weight change, %	-28.0