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Use of "Clean" Paraffinic Processing Oils to Improve TPE Properties

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Presented at TPEs 2000
Philadelphia, PA

September 27 – 28, 1999

ABSTRACT

This paper will focus on the improved TPE physical properties obtained by the use of "clean" paraffinic process oils. These oils are manufactured using a new, all-hydroprocessing technology which lowers the aromatic content of the process oils. The result is a chemically pure, practically water-white process oil with exceptional color stability and low volatility. These oils can be used in the compounding of TPEs to improve color stability, oven aging, fogging, compatibility, and other properties.

INTRODUCTION

There are three types of petroleum oils commonly used in the polymer compounding industry. These fall into the categories Paraffinic, Naphthenic and Aromatic. Generally, the Paraffinic oils are characterized by good color, good stability, good solubility or “solvent power” for saturated compounds, and higher cost. The Aromatic oils generally are characterized by poor color, poor stability, good “solvent” power for polar compounds, and lower cost. The Naphthenic oils fall in the middle between these two.

The classification system used to define process oils is ASTM D2226 and is shown in Table I. Oils are classed according to asphaltenes, polar compounds, and saturates content, with aromatics content arrived at by difference.

Table 1: Oil Classifications by ASTM D2226

Oil Type	Asphaltenes, % max.	Polar Cmpds, % max	Saturates
Aromatic			
101	0.75	25	20 (max)
102	0.50	12	20.1-35.1
Naphthenic			
103	0.3	6	35.1-65
Paraffinic			
104	0.1	1	65(min)

All oils contain aromatic and naphthenic rings. Paraffinic oils have more saturated rings and long paraffinic side chains.

The main problem with the stability of oils, and the materials that they are compounded into, involves the presence of polars and aromatics. These compounds contain impurities like nitrogen, sulfur, or oxygen which are highly susceptible to oxidation and color degradation when exposed to UV light and/or heat. Highly refined paraffinic oils have the lowest proportion of polars and aromatics and the highest proportion of saturated chains, making them the most stable oils.

There are several important criteria for selecting oils:

Color Requirements - The initial color is important when you are mixing a material that needs to be water-white. Also important is the color stability during exposure to UV light and/or heat.

Volatility Requirements - It is important that the oil is not volatile, that is, susceptible to vaporization at elevated temperatures. It therefore must not contain ingredients which “boil/vaporize” off at processing temperatures. Also, the criteria for volatility during use continue to be tightened in many applications. This is especially true in interior automotive applications. Other

applications where volatility/solubility is critical is for seals either in plumbing or electrical applications.

Compatibility or Additive Solubility - It is important that any oils used are soluble in the matrix and also that the additives do not interact with the oils.

Product Performance Properties - It is important that there is not a significant decrease in the properties of the compound after the addition of the oil.

All of these criteria are evaluated in this paper.

CRITICAL OIL PROPERTIES

The oil industry has a different language than the compounders, either rubber, plastic or TPE, are accustomed to. This paper therefore provides a brief overview of the critical oil properties. It has been recognized that the properties of an oil depend ultimately on its chemical constitution, but the analytical techniques able to provide a sufficient insight into composition have proved to be too expensive and time-consuming. Therefore, oil and rubber technologists have defined various tests and properties. These are used not only for quality control but also as a rough indicator of chemical composition.

Viscosity - This is a measure of the ability of the oil to flow at a given temperature. In general, the higher the viscosity of an oil, the higher the molecular weight.

Gravity - It is defined as the weight of oil for a given volume and is given in either API units or Specific Gravity. API is based on a hydrometer scale; specific gravity is the weight of a given volume of oil to the weight of an equal volume of distilled water - both at 60°F. This can only be used to give a very rough indication of composition since it increases with molecular weight and aromaticity.

Table 2: Typical Values for Gravity

Oil Type	API Gravity	Specific Gravity 60/60°F
Aromatic	10.0	1.000
Naphthenic	20.0	0.934
Paraffinic	30.0	0.876

Flash Point - This is the temperature of an oil when a flame will ignite vapors. It is related to the "front end" volatility of the oil. Table 3 lists a comparison of the different types of oils with the same viscosity.

Table 3: Typical Values for Flash Points

Oil Type	Viscosity	Flash Point, °F
Aromatic	3000	430
Naphthenic	3000	450
Paraffinic	3000	575

Pour Point - This is the lowest temperature at which an oil can flow. The more straight chains in the molecular structure the higher the pour point. In general, the higher the molecular weight, the higher the pour point. The lower temperature performance of a compound can be greatly influenced by the pour point of the oil used. This low temperature performance can be very critical for applications like automotive boots.

Aniline Point – This is the temperature at which equal portions of an oil and aniline are miscible. Aniline points tend to increase with molecular weight or viscosity and decrease with increasing aromatics content. Low aniline point oils tend to be compatible with most rubbers. Table 4 lists typical values.

Table 4: Typical Values for Aniline Point

Oil Type	Aniline Point Range
Paraffinic	200 - 250
Relative Naphthenic	190 - 225
Naphthenic	130 - 195
Aromatic	80 - 130

The character and quality of process oils depend on how they are manufactured. In general, there are two manufacturing routes: conventional technology, which includes solvent extraction and solvent dewaxing processes, and modern hydroprocessing technology. Many process oils are manufactured using conventional technology which leaves polar compounds and aromatics in the oil. “Clean” paraffinic process oils are made by modern, all-hydroprocessing technology which is more effective at removing polars, aromatics, and other impurities.

In hydroprocessing, undesirable components are converted to desirable and more stable molecular structures via saturation, ring opening and heteroatom removal. In hydrofinishing, the final stage of hydroprocessing, any remaining aromatics are hydrogenated, further improving oxidative stability and color. The result is a chemically pure, practically water-white, paraffinic process oil with exceptional color stability. The benefit to polymer compounders, who are constantly being challenged to reduce cost while improving product quality, is that these oils can offer the same performance as highly refined food-grade FDA/USP oil but at a much lower cost.

OILS IN TPE'S

The use of oil-extended rubber appeared in the early fifties. Oils have played an important and ever increasing role as ingredients in both natural and synthetic rubber compounds and in no small way have they contributed to the success of the synthetic rubber industry. Considerable technical and commercial benefits are attached to the use of oils in rubber compounding. First used as process aids and plasticisers and then as cheap extenders, it is now recognized that desirable service properties in a vulcanisate can sometimes only be attained with the aid of an oil.¹ In rubber, oils are used as process aids, plasticisers and extenders. Oil-extended rubbers provide a cost reduction of 10 – 15%.

With the wide use of oils in the rubber industry, it is not surprising that process oils have been used in most types of TPE's almost since their inception. With few exceptions (polyurethanes and polyamides, etc.) oils are used to vary properties. The property most commonly varied using oil is hardness. Back in 1988, the focus was to decrease the hardness of the materials being offered.² With the use of plasticizers and other aids, there are now thermoplastic elastomers with hardness around "0" Shore A.

In an early article about TPE's, the use of oil extended materials for footwear and bitumen products was recognized.³ This article shows that the more oil used, the lower the tensile properties. The oil can compensate for the addition of crystal polystyrene, which is used to increase properties.

In Thermoplastic Elastomers – A Review the use of oil was discussed.⁴ They recommend using Naphthenic oils. These oils will generally reduce tensile strength, stress at a given percent strain, tear strength, hardness abrasion resistance and melt viscosity. Also, during the initial introduction for Alcryn, the use of oils to alter final properties was discussed.⁵

The Handbook of Thermoplastic Elastomers mentions the use of plasticizers in polar TPEs but recommends paraffin-based oils and waxes for use in TPV, olefinic, and styrenic TPEs. In the compounding of styrenic block copolymers, oils have been found to decrease hardness, costs and UV resistance and increase processability.⁶

It is well documented that the oils stay in the rubber phase of the TPE.⁷ However, sometimes during the processing of the material, the oil becomes "trapped" in the plastic phase. The migration of the oil out of the plastic phase can manifest itself as an undesirable bloom. Therefore, choosing an oil with the right "compatibility factor" is critical.

Process oils have never been shown to increase properties, but using them as fillers to decrease cost has been very critical for acceptance of TPE's into the marketplace. They also serve as a great processing aid, allowing for the

addition of inorganic fillers into TPE compounding, allowing a further decrease in costs.

OILS USED FOR STUDY

Three types of paraffinic oils were compared in this study:

- oils made from the new all-hydroprocessing technology
- commonly used oils made by conventional technology
- highly refined food-grade FDA/USP mineral oil

The properties of the test oils made from the new all-hydroprocessing technology are listed in Table 5 in order of increasing viscosity. They have very good color by ASTM D1500 and no aromatics by ASTM D3238.

Table 5: Typical Properties for “Clean” all-Hydroprocessed Oils for Study

Typical Properties	Methods	Paralux 2401R	Paralux 6001R	Paralux 12001X
Viscosity @ 100°F, SUS	ASTM D2161	223	615	942
Viscosity @ 210°F, SUS	ASTM D2161	48	70	100.5
Viscosity @ 40°C, cst	ASTM D445	43.3	117.6	182.5
Viscosity @ 100°C, cst	ASTM D445	6.5	12.5	20.34
API gravity, 60°F	ASTM D287	31.8	30.3	33.7
Specific Gravity; 60°F	ASTM D1250	0.8660	0.8747	0.8565
Flash point, COC, °F	ASTM D92	453	525	554
Pour point; °C	ASTM D97	-12	-21	-38
Aniline Point, °F	ASTM D611	235	257	287**
Molecular Weight	ASTM D2502	430	582	817
Color	ASTM D1500	L0.5	L0.5	L0.5
Carbon type by ndM	ASTM D3238			
% Paraffinic Carbon		66	70	82
% Naphthenic Carb.		34	30	18
% Aromatic Carbon		0	0	0

Notes:

12001X is an experimental oil. The other two are commercially available.

**Approximate value.

The properties of the control oils are listed in Table 6 in order of increasing viscosity. The Sunpar oils represent commonly used oils made by conventional technology. The Drakeol 34 represents highly refined food-grade FDA/USP mineral oil

Table 6: Typical Properties of Control Oils for Study

Typical Properties	Methods	Drakeol 34	Sunpar 150	Sunpar 2280
Viscosity @ 100°F, SUS	ASTM D2161	390	492	2582
Viscosity @ 210°F, SUS	ASTM D2161	61.2	63.1	153

Viscosity @ 40°C, cst	ASTM D445	75.7	94.4	485.1
Viscosity @ 100°C, cst	ASTM D445	9.35	9.8	32.0
API gravity, 60°F	ASTM D287	30.8	30	27.3
Specific Gravity; 60°F	ASTM D1250	.8718	.8762	.8911
Flash point, COC, °F	ASTM D92	480	500	575
Pour point, °C	ASTM D97	-9	-15	-15
Aniline Point, °F	ASTM D611	247	245	264
Molecular Weight	ASTM D2502	492	517	776
Color	ASTM D1500	0.0	1.5	5.0
Carbon type by ndM	ASTM D3238			
% Paraffinic Carbon		68	69	69
% Naphthenic Carbon		32	30	29
% Aromatic Carbon		0	1	2

FORMULATIONS

There were a total of twelve mixes made for this study. The first six were based upon a standard SEBS formulation. The next six were based upon a standard thermoplastic vulcanizate (TPV) formulation. The formulations are shown in Table 7 and 8.

Table 7: SEBS Formulations

SEBS FORMULATION	#1	#2	#3	#4	#5	#6
KRATON G 1651	100	100	100	100	100	100
SUNPAR 150	150					
SUNPAR 2280		150				
DRAKEOL 34			150			
CHEVRON OIL – Paralux 2401R				150		
CHEVRON OIL – Paralux 6001R					150	
CHEVRON OIL - Paralux 12001X						150
POLYPROPYLENE 12 MELT HOMOPOLYMER	50	50	50	50	50	50
IRGANOX B-225	<u>0.6</u>	<u>0.6</u>	<u>0.6</u>	<u>0.6</u>	<u>0.6</u>	<u>0.6</u>
Total	300.6	300.6	300.6	300.6	300.6	300.6

Table 8: TPV Formulations

TPV FORMULATION	#7	#8	#9	#10	#11	#12
EPDM VISTALON 3708	100	100	100	100	100	100
SUNPAR 150	100					
SUNPAR 2280		100				
DRAKEOL 34			100			

CHEVRON OIL - Paralux 2401R				100		
CHEVRON OIL - Paralux 6001R					100	
CHEVRON OIL - Paralux 12001X						100
POLYPROPYLENE 12 MELT HOMOPOLYMER	40	40	40	40	40	40
VAROX DBPH 50	0.72	0.72	0.72	0.72	0.72	0.72
IRGANOX B-225	0.48	0.48	0.48	0.48	0.48	0.48
Total	241.2	241.2	241.2	241.2	241.2	241.2

All were mixed using a banbury mixer using standard conditions. They were then compression molded into plaques prior to testing.

TESTS USED FOR EVALUATION

The tests chosen for this study relate to the critical properties already discussed. All testing was accomplished according to ASTM or other industry standards.

Hardness - Hardness was tested using a Shore A durometer with a five-second delay according to ASTM D2240.⁸

Tensile Strength - Tensile strength of the samples was measured according to ASTM D412 Die C.³ Values for Ultimate Tensile Strength, Ultimate Elongation and 100% Modulus, 200% Modulus and 300 % Modulus were recorded.

Tension Set - Tension set was measured using ASTM D412.³ The samples were stretched 100% for ten minutes and then allowed to relax for 10 minutes. This value is an important measure of a material's rubber characteristic.

Compression Set - The compression set was run according to ASTM D395. This test determines elastic recovery after 168 hours of aging. The SEBS's were aged at 70 °C and the TPV's were run at 100°C.

Weight Loss in Air - The samples were weighed prior to and after aging in air for 100 hours @ 125°C. This provides a measure of the oil's volatility.

Fogging Test - The fogging test was run according to GM9305P at 110 C. In this test, a sample is placed in a beaker and covered with a glass plate. After a heating, cooling, and conditioning cycle, the fog residue that collects on the plate is measured for gloss and examined microscopically for droplets and crystals. This provides another measure of the oil's volatility and is of special interest to interior automotive applications.

Oil Transfer - The samples were tested according to ASTM D925, Method A - Contact Stain. This involves placing the specimen between a control panel and

evaluating any extrusion of oil on the surface of the specimen when aged for 48 hours @ 23°C.

Color Stability, Ultraviolet Light Exposure - The color stability of the compounds was measured according to ASTM D4329. The cycle used was 4 hours condensation and 4 hours light exposure. The samples were pulled and rated at 24, 48, 72, 168 and 240 hours. The materials were evaluated using the following criteria.

- 1 = No Staining
- 2 = Very Light Staining
- 3 = Light Staining
- 4 = Dark Staining
- 5 = Excessive Staining

Color Stability, Heat Aged – The color stability of the compounds was measured when the samples were aged according to ASTM D573 @ 125°C. The samples were pulled and rated at 24, 48, 72, 168 and 240 hours using the above rating system.

RESULTS

Hardness – The hardness for the samples tested was in the range of 47 – 57. These values fall within the published range of error for this type of equipment. There were no clear trends with any one oil providing greater softness for both types of polymer blends.

Tensile Strength – The tensile properties of the mixes do vary based upon the type of oil used. A greater variance is seen in the SEBS formulations. Formulation #3 using Drakeol 34 had the lowest tensile strength, along with the lowest percent elongation, for these formulations. Formulations using the oils with the highest molecular weight tended to have higher tensile properties.

The TPV formulations did not reach the published values for Tensile Strength, however the Elongation values are within the ranges expected. See Figures A and B.

Tension Set – The tension set values for all of the materials are reasonable, as shown in Figure C. The inclusion of harmful materials would greatly decrease these values. This analysis shows that none of the oils evaluated contain many harmful contaminants.

Compression Set – More elastic recovery occurs with the TPV's. Over both formulations recover decreases with increasing viscosity of the oil. See Figure D.

Weight Loss in Air – The values obtained for weight loss are shown in Figure E. The weight loss in air is slightly related to the molecular weight of the oil as calculated via regression analysis. Only the Paralux 2401R, one of the new hydroprocessed oils, had any significant weight loss. However, this oil had the lowest viscosity and lowest flash point of all the oils tested. The rest had minimal weight loss.

Fogging- The fogging numbers are shown in Figure F. The least amount of fogging, or volatile material collected, occurs with the higher viscosity oils.

Oil Transfer – None of the materials showed the presence of oil transfer. This served as a check on the mixing process. It also showed that the oil must have been correctly incorporated into the rubber phase of the compounds.

Color Stability, Ultraviolet Light Exposure – The really critical data from this study is in the Color Stability portion. The color stability after Ultraviolet Light exposure is shown in Figure G. The discoloration in these samples was definitely visible to the naked eye. Of course, some of the samples started out dark to begin with, but the ones rated with a value of 2 showed only a very slight discoloration.

Most of the samples showed an initial discoloration after 24 hours with no further change in color past that aging time. Overall, the all-hydroprocessed oils performed as well as the FDA/USP oil. The conventionally produced process oils had a significant amount of discoloration.

Color Stability, Heat Aged – The heat aging had a slightly different effect than the UV Light exposure, but the effect was very visible for only some of the oils. This is shown in Figure H. In all cases the discoloration was more noticeable on the TPV rather than the SEBS formulations. Again, the all-hydroprocessed oils performed as well as the FDA/USP oil and better than the conventionally produced oils. Also formulation # 6 using Paralux 12001X did not experience any discoloration, even after 240 hours.

A regression analysis was accomplished on most of the data with comparison to the original properties. In almost all cases, there was no link between the original properties and the data obtained. This is definitely because there are more factors at play than one simple property measurement.

CONCLUSIONS

“Clean” paraffinic process oils made using all-hydroprocessing technology have excellent compatibility with rubber polymers and perform as well as conventionally produced process oils in TPE products. This means they can be

easily dropped into existing formulas, physical properties will remain constant, and several benefits will be realized:

- Most important is the good initial color and the lack of discoloration after UV and/or heat exposure. For applications such as consumer articles, lightly colored items, sporting goods, etc. where food grade or medicinal oils are not required, these oils perform as well as FDA/USP oil, at lower cost.
- The weight loss is very low. This results in fewer emissions and is important in applications where fogging or flexibility retention are important.
- In some cases, the tension set is improved.

¹ Rubb. J. 154, No. 5, May 1972, p. 35-52.

² Plast. Tech. Aug. 1988, p 44-51.

³ Eur. Rubb. J. 161, No. 6, July 1979, 15/21.

⁴ Thermoplastic Elastomer – A Review of Current Information, A.D. Thorn, 1980, p 64.

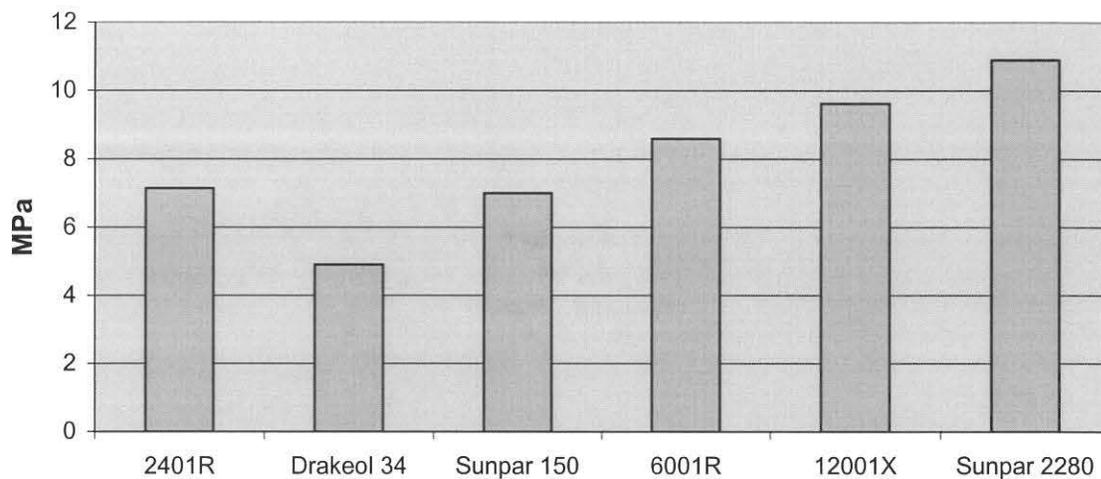
⁵ Eur. Rubb. J. 167, No. 5, May 1985, p. 9.

⁶ Handbook of Thermoplastic Elastomers, Ed. B. Walker and C. Rader, 2nd Ed., p. 374.

⁷ Handbook of Thermoplastic Elastomers, Ed. B. Walker and C. Rader, 2nd Ed., p. 51.

⁸ ASTM 9.01.

**Figure A-1
SEBS
Tensile Strength**



**Figure A-2
TPV
Tensile Strength**

