

## **An Evaluation of Sebacic Acid and Azelaic Acid as Thickeners in Lithium Complex Greases**

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Published in the NLGI Spokesman, Vol. 72, No. 4, July  
2008

## **Abstract**

Azelaic acid, the C<sub>9</sub> dicarboxylic acid, has long been the thickener of choice in lithium complex greases. Sebacic acid, the C<sub>10</sub> analog, has enjoyed a minor share in this application. Recent structural changes in the sebacic acid market in the US have made sebacic acid much more attractive as an alternative to azelaic acid. This paper compares the performance of sebacic and azelaic acids when used as thickeners in both polar polyol ester and non-polar PAO basestocks.

## **Introduction**

Lithium complex greases represent some 35% of greases produced in North America and a lesser but still important proportion elsewhere in the world.<sup>1</sup> The diacid component of the thickener typically comprises 2-5% of the formulation and is responsible for the differentiating performance attributes of this class of greases.<sup>2</sup> Adipic acid (C<sub>6</sub>), azelaic acid (C<sub>9</sub>) and sebacic acid (C<sub>10</sub>) have all been used as the diacid component for a number of years with azelaic acid being the workhorse thickener.<sup>3</sup> Figure 1 shows the comparative physical properties of sebacic acid azelaic acids.

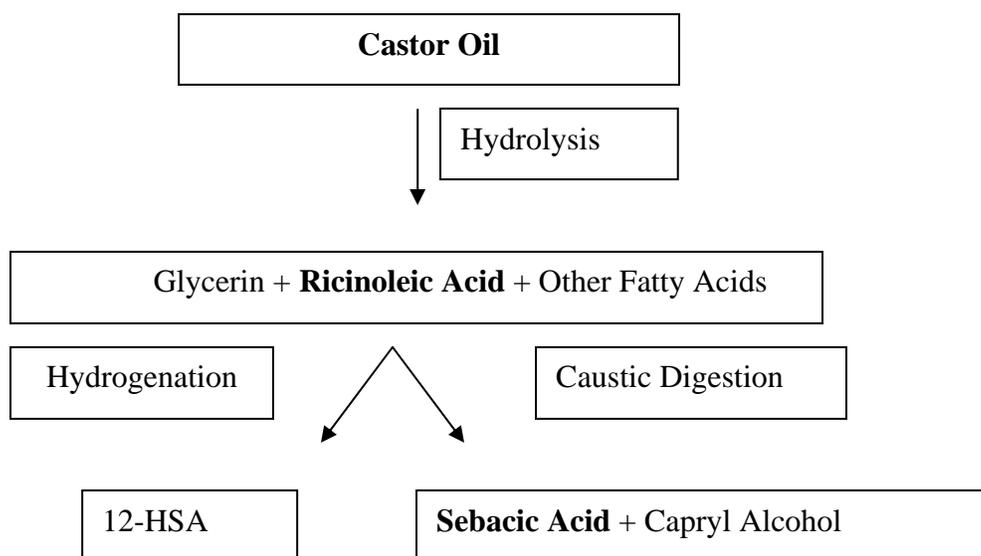
<p><b><u>Sebacic Acid</u></b>            HO<sub>2</sub>C(CH<sub>2</sub>)<sub>8</sub>CO<sub>2</sub>H            CAS 111-20-6            MW 202.3            MP 131-134°C            Purity 99.5% min            Water Solubility                1g/L @ 17°C                20g/L @ 100°C            LD50 (rat) 3.4 g/kg</p>	<p><b><u>Azelaic Acid</u></b>            HO<sub>2</sub>C(CH<sub>2</sub>)<sub>7</sub>CO<sub>2</sub>H            CAS 123-99-9            MW 188.2            MP 98-103°C            Purity 85-90%            Water Solubility                2.4g/L @ 20°C              LD50 (rat) &gt;5 g/kg</p>
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**Figure 1: Comparative Properties of Sebacic Acid and Azelaic Acid**

Sebacic acid is a widely-used industrial intermediate with an annual global demand of around 20,000 metric tons. In addition to its application in greases, sebacic acid is a key intermediate for nylon 6/10 resins used in engineering plastics, polyester polyols used in reactive hot-melt polyurethane adhesives and as a corrosion inhibitor in metalworking fluids and long-life anti-freeze formulations. Sebacic acid is also used as a raw material for disodium sebacate (DSS). DSS is approved for use in greases for incidental food contact under CFR 21.178.3570. Sebacate esters are also widely used, finding application as low-temperature plasticizers and synlube basestocks and in the cosmetics market as emollients and fragrance carriers. As with azeleate esters, the sebacate esters are frequently used as liquid proxies for the corresponding acid in making greases.

Both sebacic acid and azelaic acid are derived from oleochemical sources. Azelaic acid is produced via the ozonolysis of oleic acid with pelargonic acid (n-nonanoic acid) as a co-product. The majority of the azelaic acid production is out of a single facility in North America. The emergence of the biodiesel industry in North America, Europe and Asia has significantly increased the industrial demand for soy and corn oils, the principle sources of oleic acid. This has exerted upward price pressure on the key raw materials for azelaic acid.

Sebacic acid is a castor bean derivative. It is produced via the alkaline digestion of ricinoleic acid (12-hydroxy-9-octadeceneoic acid), which is the primary fatty acid component of castor oil. In addition to being the raw material for sebacic acid, ricinoleic acid is an important base material for the grease industry as it yields 12-hydroxystearic acid (12-HSA) upon hydrogenation.



**Figure 2: Sebacic Acid Manufacturing Process**

India is the world's primary source of castor bean production with China and Brazil as secondary producers.<sup>4</sup> China dominates world sebacic acid production with only one production site operating outside of China at this time. There was domestic US production operating until 2004-2005. Up until that time, sebacic acid prices in the United States were held artificially high relative to the rest of the world because of an anti-dumping duty. That duty has since been rescinded and US pricing is harmonizing with the rest of the world. As a result, the price differential between sebacic acid and azelaic acid has been widening, prompting many in the grease industry to reevaluate sebacic acid as an alternative to azelaic acid in lithium complex greases.

### **Experimental**

The purpose of this study was to compare the performance of sebacic and azelaic acids in both non-polar and polar basestocks. Four lithium complex greases were prepared. Two greases were formulated using sebacic acid as the complexing agent while two other greases were formulated

using azelaic acid as the complexing agent. Of the two greases formulated with each dicarboxylic acid, one was prepared from synthetic hydrocarbon base fluid (80% PAO-6 + 20% alkylated naphthalene) and the other from a polyol ester (Lexolube® 68-HT (Inolex Chemical Company)). These base fluids, possessing wide differences in polarity, were selected to demonstrate the utility of the acids to produce grease in a broad range of oils. Laboratory size batches of grease were prepared and tested for chemical and physical properties. Physical properties of the base fluids are compared in Figure 3.

<b>Table 1: Basestock Properties</b>		
<b>Property</b>	<b>PAO</b>	<b>Polyol Ester</b>
Tradename	Synfluid® PAO-6	Lexolube® 68HT
Producer	Chevron Phillips Chemicals	Inolex Chemical Company
Viscosity (cSt @ 40°C)	30.5	68
Viscosity (cSt @ 100°C)	5.8	9.6
Viscosity Index	135	131
Pour Point (°C)	-78	-37
Flash Point, COC (°C)	238	284

The alkylated naphthalene basestock had a kinematic viscosity of 29 cSt at 40°C and 5 cSt at 100°C.

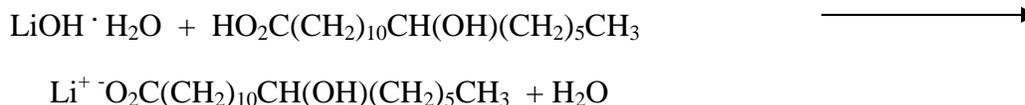
### **Synthetic Hydrocarbon Greases**

A twenty five hundred gram batch of synthetic hydrocarbon base grease containing 20% thickener was prepared in the laboratory using a two step neutralization procedure. The synthetic hydrocarbon base stock comprised a mixture of 80% PAO-6 and 20% alkylated naphthalene. A stoichiometric amount of lithium hydroxide monohydrate was first reacted with 12-hydroxystearic acid followed by the reaction of a slight excess of base with the dicarboxylic acid. Details of the procedure and chemistry are illustrated for the preparation of the lithium complex grease based on sebacic acid and the synthetic hydrocarbon base oil.

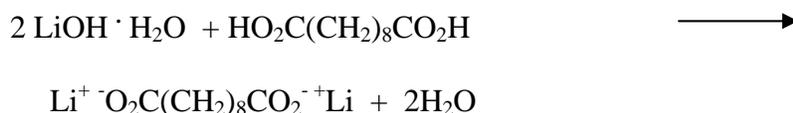
Reaction sequence for the two stage reaction of base with fatty acids:

1. React  $\text{LiOH} \cdot \text{H}_2\text{O}$  with 12-HSA
2. React  $\text{LiOH} \cdot \text{H}_2\text{O}$  with  $\text{C}_{10}$  Diacid

Step 1:



Step:2



Ingredient	FW/MW	Comments
LiOH · H <sub>2</sub> O	41.9 g mole <sup>-1</sup>	Base
12-HSA	300	C <sub>18</sub> carboxylic acid
Li 12-HSA	306	Thickener
Sebacic Acid	202	C <sub>10</sub> dicarboxylic acid
Li Sebacate	213.8	Co-thickener

Predetermined thickener ratio: 73% Li 12-hydroxystearate and 23% Lithium Sebacate

500g x 0.73 = 365 g required of Li 12-HSA Moles = 365g/305.9 g/mole =1.19 moles

500g x 0.23 = 135g required of Li Sebacate Moles = 135g/213.9 g/mole = 0.63 mole

Ingredient	Moles	FW/MW	Grams Required
LiOH · H <sub>2</sub> O	1.19	41.9	49.9
12-HSA	1.19	300	357.9
LiOH · H <sub>2</sub> O	0.63 x 2	41.9	52.7
C <sub>10</sub> Acid	0.63	202	127.3

#### Procedure:

1. The laboratory vessel was charged with 1000 grams of the base oil and all of the 12-HSA followed by the lithium hydroxide monohydrate required for step 1 dissolved in approximately 100 ml of deionized water.
2. The reaction was allowed to proceed while being heated to about 100°C under constant mechanical agitation.
3. When the neutralization of the 12-HSA appeared complete and the thickener had formed, the sebacic acid was added to the vessel followed by the required base for Step 2.
4. The reaction was allowed to proceed while the temperature was gradually increased to 200°C. to facilitate dehydration of the vessel charge.
5. Upon reaching a temperature of 200-210°C, the vessel contents were rapidly cooled by addition of the balance of the base fluids.
6. Post reaction processing consisted of homogenizing the base grease at 6000 psi.
7. The grease was brought into grade using additional base oil and subsequently fortified with additives.
8. The composition of the grease appears in Table 2.

<b>Table 2: Synthetic Hydrocarbon Base Grease Composition</b>		
<b>Ingredient</b>	<b>Weight %</b>	<b>Function</b>
Lithium Complex Base	76.0	
Base Oil (80/20)	18.4	Adjust Consistency
Phosphate Ester	3.0	Boundary Additive
Borate Additive	1.5	Load Carrying Capacity
Phenolic Antioxidant	0.5	Oxidative Stability
Amine Antioxidant	0.5	Oxidative Stability
Alkylated Benzotriazole	0.1	Copper Passivation

Note: After the base grease was adjusted to an NLGI Grade 2 consistency, the grease was re-homogenized at 6000 psi.

Both greases were formulated with the same additive package.

The chemical and physical properties of the greases are reported in Table 3 and samples can be seen in Figure 3.

<b>Table 3: Properties of Synthetic Hydrocarbon Based Greases</b>			
<b>Property</b>	<b>Procedure</b>	<b>C<sub>10</sub> Grease</b>	<b>C<sub>9</sub> Grease</b>
% Thickener	Calculated	15.2	15.4
% Dicarboxylic Acid	Calculated	4.1	4.2
Base Fluid	Report	SHC	SHC
Color	Visual	Light Tan	Tan
Appearance	Visual	Smooth	Smooth
Po	ASTM D217	296	282
P60		294	294
P10K		320	333
NLGI Grade		2	2
Oil Separation 24h at 100°C	ASTM D6184	1.8%	2.2%
Evaporation, 24h at 100°C	Internal Method	0.4%	0.7%
Dropping Point	ASTM D2265	> 260°C	> 260°C
Copper Corrosion, 24h at 100°C	ASTM D4048	1b	1b
Thermooxidative Stability	ASTM D5483 (mod)	74 min.	46 min.
Thermogravimetric Analysis	Internal Method	270°C Onset	273°C Onset
Low Temperature Apparent Viscosity	Brookfield	5.2 x 10 <sup>6</sup> mPa.s	4.4 x 10 <sup>6</sup> mPa.s
Wear Characteristics	ASTM D2266	0.39 mm	0.45 mm
Water Washout, 79°C	ASTM D1264	16.0%	36.4 %
Density, 25°C	Internal Method	0.83 g/cc	0.83 g/cc
Chemistry	FT-IR	See Spectrum	See Spectrum

Notes:

The thermooxidative stability was determined using a modified ASTM D5483 procedure on a TA Instruments Q10 Model Pressure Differential Scanning Calorimeter. Testing was conducted

at 3500 kPa using dry, pure oxygen. Aluminum Soluble Fat Index (SFI) pans were used to contain grease samples. The temperature was ramped to 210°C at 60°C per minute.

Low temperature apparent viscosity was determined using a Brookfield DV3+ viscometer fitted with a T-C spindle rotating at 1 RPM. A computer program measured apparent viscosity a 5 minute intervals while temperature was monitored with an RTD probe mounted in close proximity to the rotating spindle. The viscometer was mounted atop of a Tenney environmental chamber while the spindle was inserted into the grease through a port specially cut into the top of the chamber. The chamber temperature was set at minus 45°C and viscosity readings were recorded over a three hour interval. Three hours are usually sufficient to provide a comprehensive rheogram of grease rheology as a function of decreasing temperature.

The lighter color of the C<sub>10</sub> based grease is the result of less time being required to affect grease formation. Although a N<sub>2</sub> purge would eliminate the color difference, the C<sub>10</sub> dicarboxylic acid appears to require less heating to form grease in synthetic hydrocarbon and ester base stocks.

### Ester Greases

The ester basestock chosen was Lexolube® 68HT, a proprietary polyol ester formulation manufactured by Inolex Chemical Company. Properties of the ester are given in Table 1.

The two ester based greases were formulated using a slightly different strategy for the reaction of the base with the carboxylic acids. Since esters are prone to base-catalyzed saponification, the neutralization reaction was conducted in a small amount of synthetic hydrocarbon fluid. Moreover, the dicarboxylic acid was reacted first and preformed lithium 12-hydroxystearate was used to complete thickener preparation. This procedure was used since only 200g of hydrocarbon oil was used as the medium for acid/base neutralization.

The procedure was necessary to reduce the intractability of the thickener under lab conditions. The soap mass could be cut back with polyolester sooner in the grease preparation sequence.

The composition of the lithium complex ester grease based on sebacic acid is reported in Table 4 and the samples can be seen in Figure 4. The same additive package was used for both the sebacic acid and azelaic acid based greases.

<b>Table 4: Ester Based Lithium Complex Grease – Sebacic Acid Thickener</b>	
<b>Ingredient</b>	<b>Weight %</b>
Base Grease	61.4%
Polyol Ester Fluid	34.5
Phosphate Ester	3.0
Amine Antioxidant	1.0
Copper Passivator	0.1

Table 5 summarizes the test results for the ester greases. The test methods used were the same ones referenced in Table 3.

**Table 5: Properties of Polyol Ester Based Greases**

Property		C <sub>10</sub> Ester	C <sub>9</sub> Ester
% Thickener	Calculated	17%	17%
% Dicarboxylic Acid	Calculated	4.6%	4.6%
Base Fluid	Report	Lexolube®68-HT	Lexolube®68-HT
Color	Visual	Light Beige	Light Beige
Appearance	Visual	Smooth	Smooth
Po	ASTM D217	290	294
P60		290	307
P10k		327	334
NLGI Grade		2	1.5
Oil Separation	ASTM D6184	1.8%	2.6%
Evaporation	Internal Method	0.6%	None
Copper Corrosion	ASTM D4048	1b	1b
Dropping Point	ASTM D2265	215°C	215°C
Apparent Visc. -40°C	ASTM D5483 (mod)	4.6 x 10 <sup>6</sup> mPa.s	1.1 x 10 <sup>6</sup> mPa.s
Oxidative Stability	Brookfield	34.5 min.	26.6 min.
TGA	Internal Method	346°C Onset	346°C Onset
Wear	ASTM D2266	0.63 mm	0.68 mm
Water Washout, 79°C	ASTM D1264	8.0 %	5.7%
Chemistry	FT-IR	See Spectrum	See Spectrum

The dropping point for both greases was lower than expected. While there are insufficient data to draw a firm conclusion, it is possible that the effect is due to combination of the need to use a pre-formed soap with the small preparative scale. It is important to note that the same effect was observed with both the C<sub>9</sub> and C<sub>10</sub> greases. Thus it appears to be an artifact of the process rather than due to the choice of complexing agent.

### Conclusion:

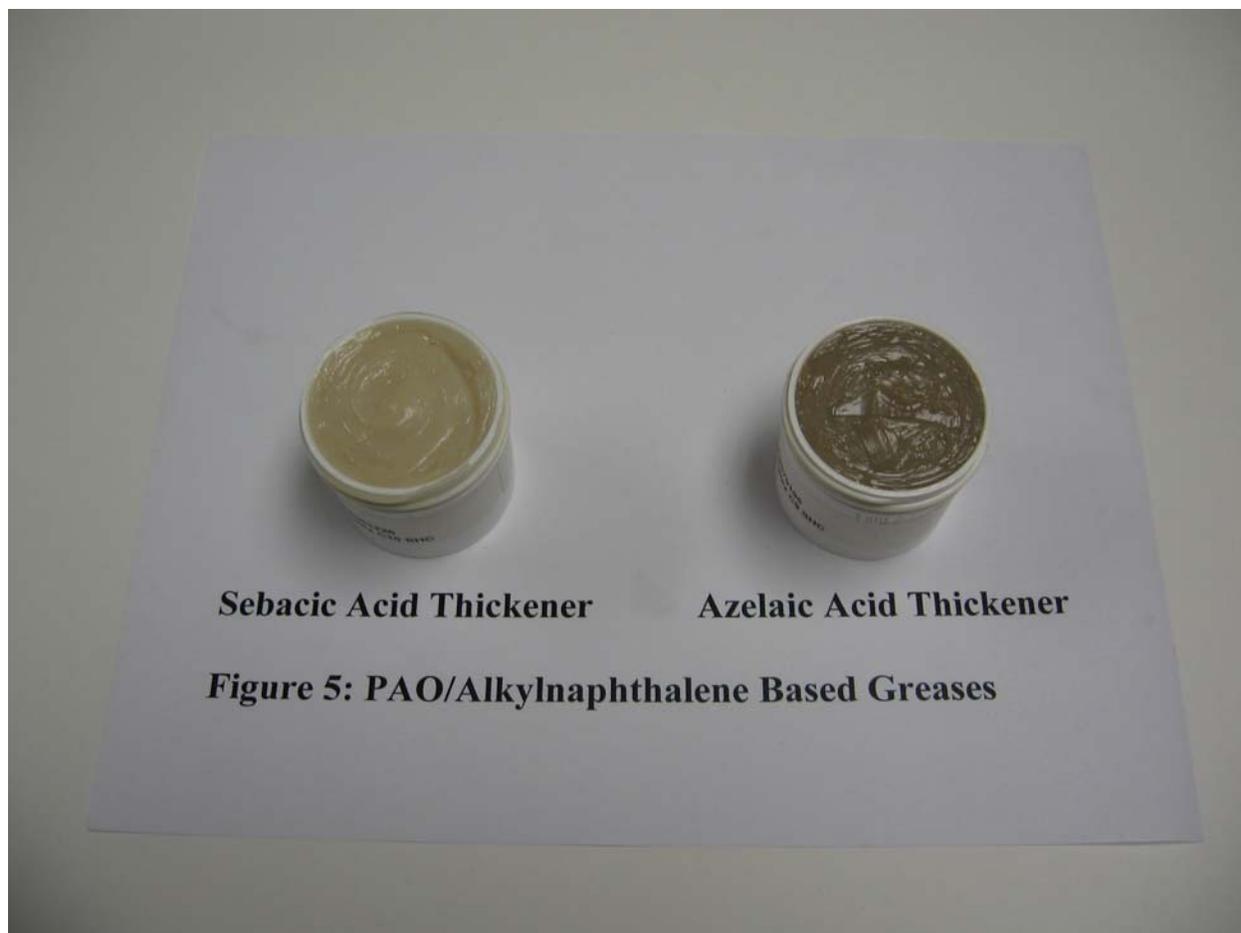
Sebacic acid is a viable complexing agent for the preparation of lithium complex grease in synthetic hydrocarbon and polyol ester base fluids.

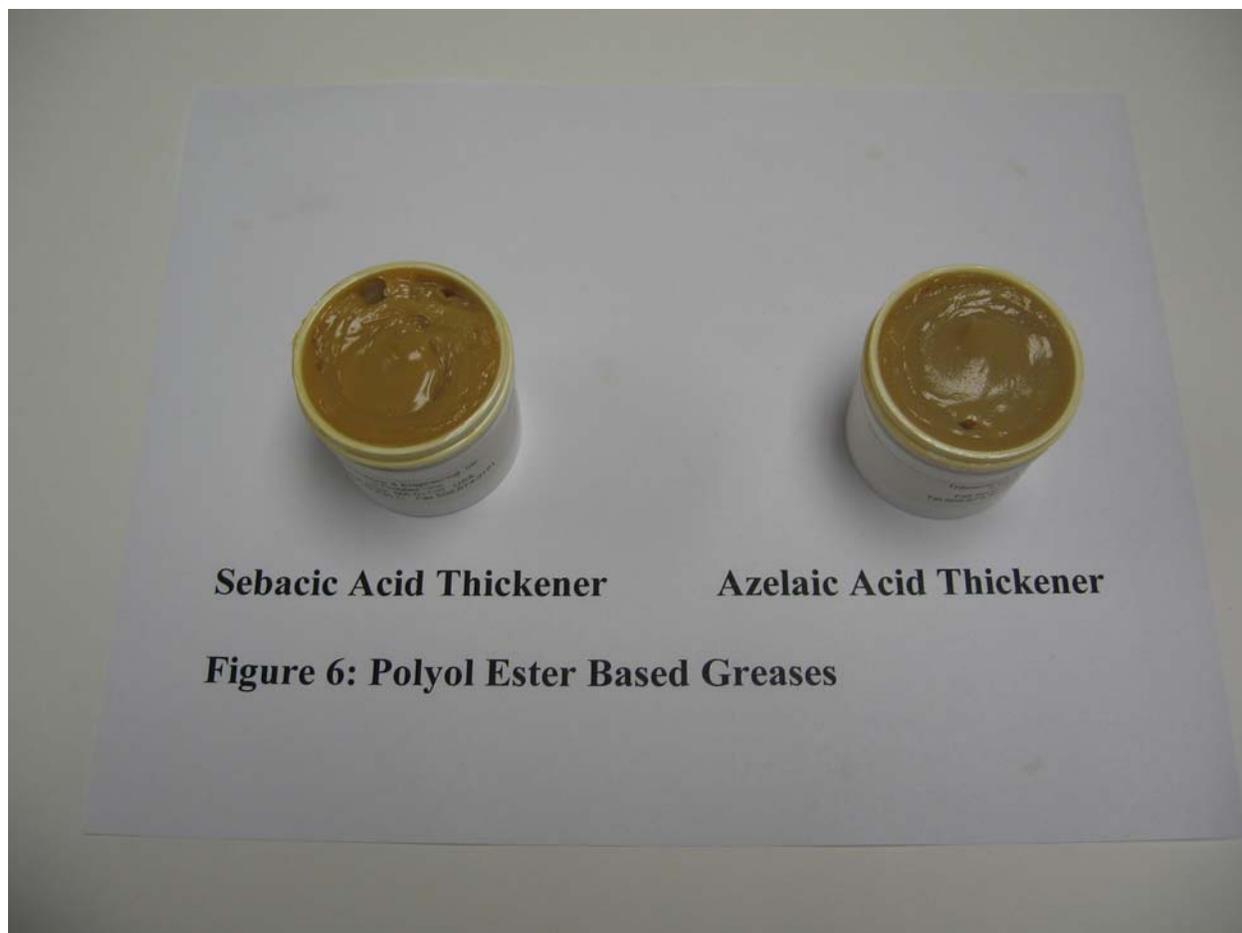
The physical properties of synthetic hydrocarbon based lithium complex grease formulated with sebacic acid are similar to those of grease made with azelaic acid. The C<sub>10</sub>- based grease exhibited better thermooxidative stability per PDSC and slightly poorer performance in low temperature apparent viscosity.

The C<sub>10</sub> acid appears to facilitate the grease making process. This may be due to the more homogenous composition of the C<sub>10</sub> carboxylic acid. After neutralization and subsequent cooling to affect thickener formation, the sebacic acid based greases possessed a smoother appearance. Homogenization at 6000 psi eliminated the difference in appearance of the base greases.

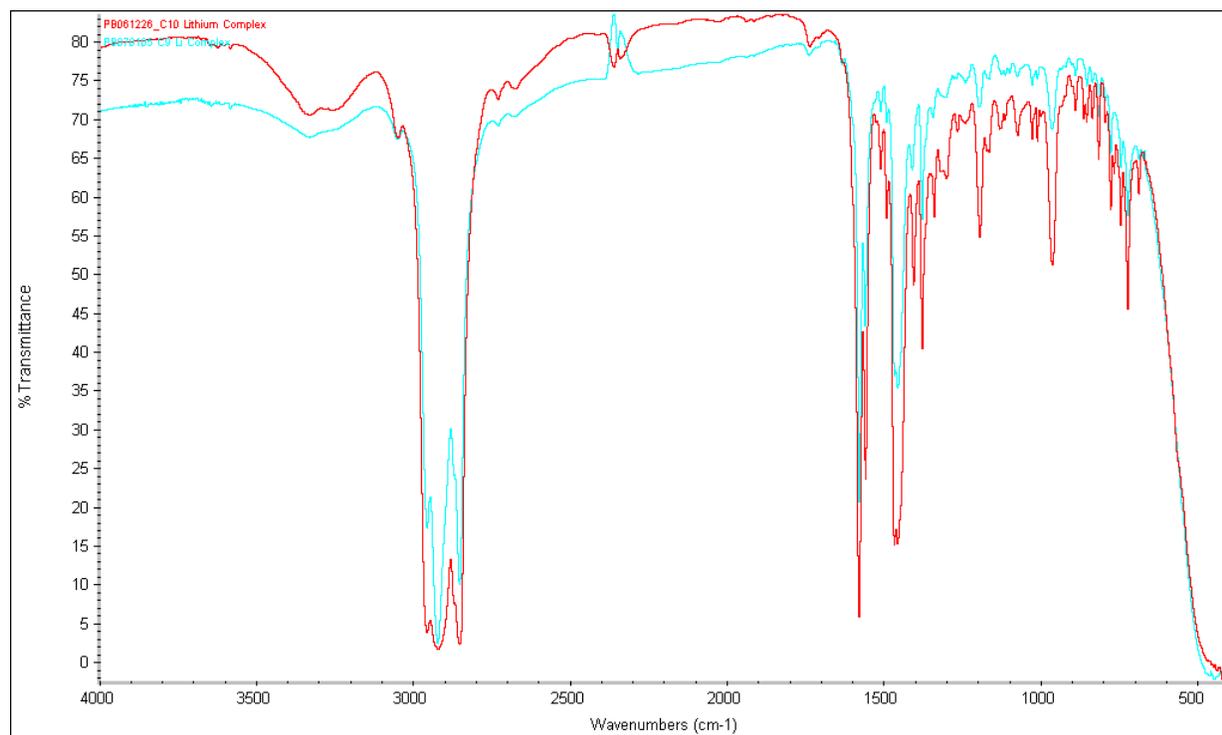
### References:

- 1: NLGI Production Survey , October 2006
- 2: See: Polishuk, Arthur T, *A Brief History of Lubricating Greases*, Llewelyn & McJane inc. (1998), Chapter 12.
- 3: US 2,699,428 (Jan. 11, 1955); US 2,898,296 (Aug. 4, 1959) and numerous subsequent patents.
- 4: See [www.castorworld.com](http://www.castorworld.com) for background about castor oil, its production and applications.



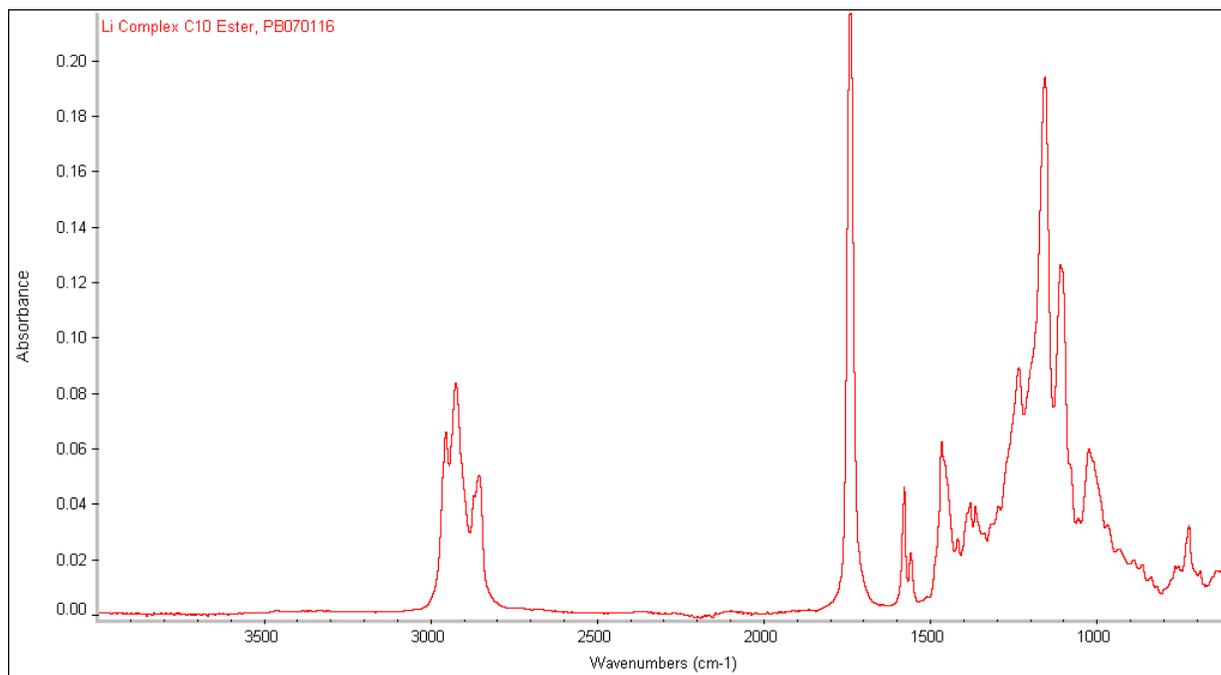


## FT-IR Spectra

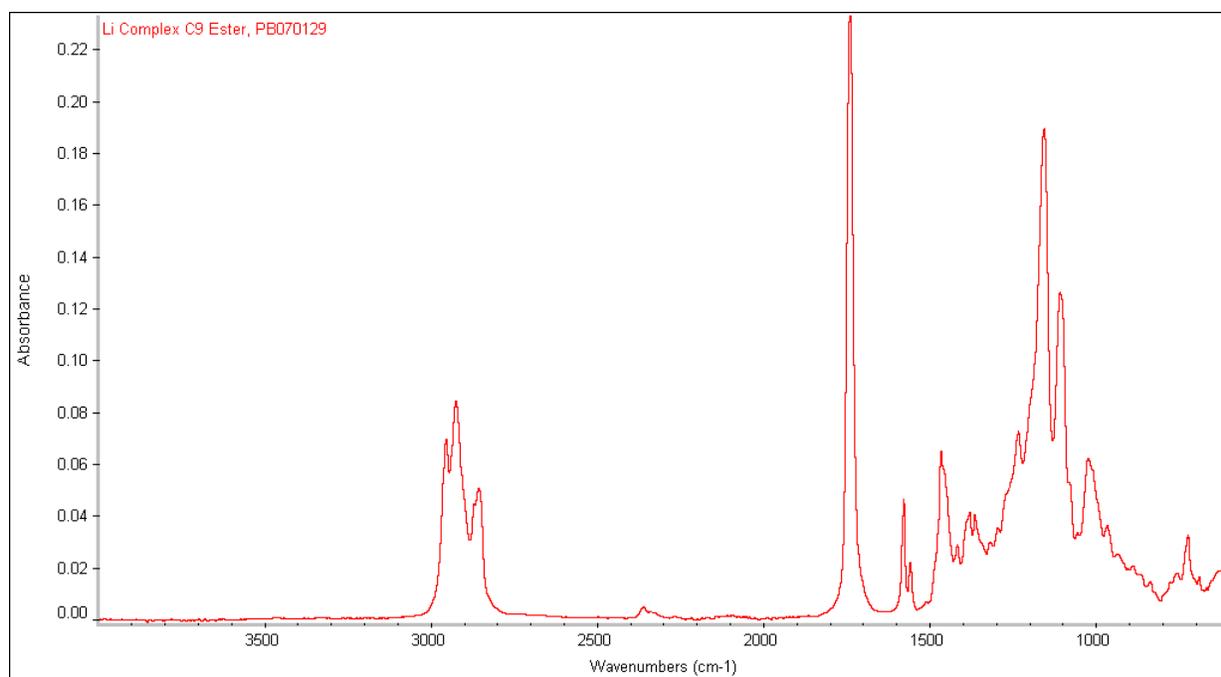


Red Spectrum = C<sub>10</sub> Lithium Complex w/ SHC's  
Blue Spectrum = C<sub>9</sub> Lithium Complex w/SHC's

### FT-IR Spectrum of Lithium Complex C<sub>10</sub> Polyol Ester



### FT-IR Spectrum of Lithium Complex C<sub>9</sub> Polyol Ester



### Spectral Overlap of C10 and C9 Ester Grease

