Lube-Tech
PUBLISHED BY LUBE: THE EUROPEAN LUBRICANTS INDUSTRY MAGAZINE
No.115 page 1

The Effect of Base Oils on Thickening and Physical Properties of Lubricating Greases

Edward Casserly, *Ph.D.*, **Timothy Langlais**, *MBA, and*
Staci P. Springer, *MBA, ERGON REFINING, Inc., Jackson, MS*

in cooperation with
Anoop Kumar, *Ph.D. and Bill Mallory, Royal Manufacturing Company, Tulsa, OK*

This paper examines the effects of naphthenic, paraffinic, and synthetic (polyalphaolefin or PAO) base oils on the thickening capabilities of lithium 12-hydroxystearate (Li 12-HSA), lithium complex (Li complex), aluminum complex (Al complex), clay base, and calcium sulfonate complex (Ca sulfonate) greases and their associated physical properties.

Introduction

Lubricating greases consist of base oil (50-98%), thickener (2-50%), and various additives (0-10%) such as antioxidants, corrosion inhibitors, antiwear, and extreme pressure additives. Grease may be used to lubricate bearings and gears (enclosed and open), provide a protective coating, or as a parting agent and drawing compound in casting. Grease is used instead of oil in applications where retention is important, less frequent application is required, to seal out dirt and contaminants, and to protect metals from corrosion.

Accordingly, manufacturers measure several unique physical properties of grease: pumpability, dropping point, mechanical stability, and oil separation. In general, for most soap-thickened greases, base fluid viscosity and grease consistency are independent properties of a lubricating grease. The viscosity of the base fluid is determined by the base stock viscosity as well as the effect of some additives. The consistency of a grease is determined by the type and concentration of the thickener in the product.

There are three basic types of hydrocarbon base oils used in grease today. These are naphthenic oils, paraffinic oils, and synthetic isoparaffinic hydrocarbons. The paraffinic oils can be further subdivided into Group I, Group II, and Group III base oils. The synthetic isoparaffinic hydrocarbons consist of Group IV polyalphaolefins (PAO) which are typically oligomers of 1-decene and are the most widely used synthetic hydrocarbons for lubricant applications, and other types of synthetics including Group V polyisobutenes (PIB), which are oligomers of isobutylene, and esters, primarily dibasic esters or polyol esters. PAO remains the only synthetic base oil evaluated in this study.

Up until the '90s, most paraffinic oils were Group I oils. In response to increasing regulation and technical demands placed on automotive engine oils (e.g., fuel economy and emissions), the industry moved from solvent-refined Group I base oils to hydroprocessed Group II and III base oils. In contrast to Group I, naphthenics (Group V) can be produced via solvent extraction or hydroprocessing. Today's state-of-the-art naphthenic refineries use severe hydroprocessing to produce high-quality "clean" or low PAH (polycyclic aromatic hydrocarbon) naphthenic base oils that have reduced sulfur content and lower PAH content while preserving valuable solvency characteristics.

Group I base oils contain a considerable amount of sulfur and saturates of less than 90%. While most commercially available Group II and Group III base oils have essentially no aromatic content, Group I and severely hydroprocessed naphthenic base oils have been processed to remove the PAHs while leaving other aromatics intact. The removal of the PAHs is necessary to produce a "clean" base oil that meets the Health, Safety, and Environmental (HSE) regulations of the applications for which they are used.

Solvency is affected most by the aromatic content and then by the naphthenic (i.e., saturated ring structures) content. As the aromatic content decreases, the solvency decreases, and as the naphthenic content increases, the solvency increases. When aromatics are hydroprocessed, they are converted to naphthenes. Therefore, to maintain solvency after reducing the amount of PAHs for HSE requirements, naphthenics are an outstanding way to increase the solvency of a lubricant formulation.

Solvency is impacted by several somewhat related factors and can be assessed in terms of aniline point, viscosity index (VI), and viscosity-gravity constant (VGC). Aniline point, ASTM D611, characterizes solvency via a compatibility test between the oil and aniline, which is an aromatic amine. The aniline point is defined as the minimum equilibrium solution temperature for equal volumes of aniline and the oil sample. The more soluble the oil is in the aniline, the lower the temperature required for the oil and aniline to become miscible. Less soluble oils require higher temperatures. This is an example of the industry adage, "like dissolves like." Aniline is a polar molecule, and polar base oils are more readily miscible with aniline at a lower temperature. The lower the aniline point, the higher the solvency of the base oil.

The viscosity index (VI), ASTM D2270, which is a dimensionless number, is used to characterize the variation of the kinematic viscosity of a petroleum product with temperature. The higher the VI number, the less change in viscosity due to temperature. The VI correlates with chemical structure, with aromatics having the lowest VI, then naphthenics, and paraffins having the highest VI; therefore, a higher VI indicates a lower solvency.

Viscosity-Gravity Constant (VGC), ASTM D2501, describes the general relation between specific gravity and Saybolt viscosity. The VGC is low for paraffinic (0.800) and high for aromatic (1.00) type oils. As the VGC increase, the solvency increases. VGC is often used in conjunction with aniline point since VGC is independent of molecular weight.

The thickener in a lubricating grease is the component that sets grease apart from fluid lubricants. Thickeners are molecules, polymers, or particles that are partially soluble in lubricating fluid; they arrange themselves in such a way that they impart a semi-solid consistency to the grease. Many different types of chemical compounds can be used to thicken grease.

The amount of thickener used during manufacture is linked to the desired physical properties of a finished grease. Since the soap or clay is typically more expensive than the base oil, minimizing the soap or clay content while maintaining the physical properties is paramount. The amount of thickener necessary to form the microstructure depends on the interactions between the thickener and the base oil, which depend on the solvency of the base oil. The higher the solvency, the more the interaction and the less thickener required to produce a grease with the targeted NLGI grade, which ultimately lowers the overall formulation cost.

Simple soaps are the most common grease thickeners. A simple soap is the reaction product of an organic acid (long-chain or fatty carboxylic acid) and an alkali metal to form an organic salt. Thus, simple soap is an acid-base reaction product. This reaction is called saponification. Simple soaps are most commonly based on salts of lithium and calcium, and less commonly on salts of sodium, aluminum, and barium. Examples of simple soap thickeners include lithium 12-HSA and calcium stearate.

Complex soaps are also used widely as grease thickeners. The term "complex" refers to the combination of a simple soap and a complexing agent. For example, a lithium complex thickener typically contains lithium 12-HSA (simple soap) and a salt of a shorter chain difunctional carboxylic acid, boric acid, or an aromatic acid (complexing agent). Complex thickeners are usually based on lithium, calcium, or aluminum compounds. Grease can also be thickened with non-soap materials. Common non-soap thickeners include polyurea, clay, fumed silica, fluoropolymers, and others.

Clay thickeners include the minerals bentonite and hectorite. These minerals are purified to remove any non-clay material, ground to the desired particle size distribution, and then chemically treated to make the particles organophilic (more compatible with organic chemicals). Clay particles are then dispersed in a fluid lubricant to form grease. Clay particles must be activated with a polar material to stabilize the thickener structure. Clay thickeners have no defined melting point, so they have been used historically in high temperature applications operating up to 200°C, such as kilns and drier ovens.

For this study, we will examine the differences between several naphthenic and paraffinic base oils, a PAO, and a bright stock as they relate to processing and properties of Li 12-HSA, Li complex, Al complex, Ca sulfonate and clay based greases.

Design of experiment

In this study, NLGI Grade 2 greases were prepared using five different thickener systems:

1) lithium 12-hydroxystearate (Li 12-HSA)
2) lithium complex (Li complex)
3) aluminum complex (Al complex)
4) calcium sulfonate (Ca sulfonate)
5) clay

Seven base oils with different aniline points were used with each type of thickener:

- 150 N1 - Group V naphthenic base oil, ISO VG 150, 197.5°F (91.9°C)
- 150 N2 - Group V naphthenic base oil, ISO VG 150, 191.3°F (88.5°C)
- 460 N3 - Blend of 150 N1 and 1000 P3, ISO VG 460, 231.5 °F (110.8°C),
- 1000 P3 - Group I bright stock, ISO VG 1000, 248.5°F (120.3°C)
- 100 P1 - Group I paraffinic base oil, ISO VG 100, 248°F (120°C)
- 100 P2 - Group II paraffinic base oil, ISO VG 100, 256.8°F (124.9°C)
- 150 S1 - Group IV PAO base oil, ISO VG 150, >300°F (>148.9°C)

The physical properties of the base oils are given in Table 1.

Generic Name	150 N1	150 N2	460 N3	1000 P3	100 P1	100 P2	150 S1
Description*	Group V Nap	Group V Nap	Nap/Par Blend	Group I BS	Group I Par	Group II Par	Group IV PAO
ISO VG	150	150	460	1000	100	100	150
Vis 40°C, cSt	143.99	142.90	475.34	958.24	106.10	117.30	148.47
Vis 100°C, cSt	11.04	10.50	26.36	43.04	10.90	12.10	21.19
Viscosity Index	39	25	72	82	84	92	168
Aniline Pt, °F (°C)	197.5 (91.9)	191.3 (88.5)	231.5 (110.8)	248.5 (120.3)	248 (120)	256.8 (124.9)	>300 (>148.9)
Viscosity-Gravity Constant (VGC)	0.853	0.832	0.832	0.819	0.799	0.799	0.765
Specific Gravity, 60/60°F	0.9170	0.9017	0.9151	0.9141	0.8737	0.8756	0.8536
Carbon Type, D2140							
$\%C_A$	11.3	19.7	9.3	7.4	0.6	0.0	0.0
$\%C_N$	37.7	14.2	31.2	26.6	30.0	32.8	20.2
$\%C_P$	51.0	66.1	59.5	65.9	69.4	67.2	79.8
Refractive Index	1.5028	1.5052	1.5028	1.5027	1.4798	1.4791	1.4646

* Nap = Naphthenic; Par = Paraffinic; BS = bright stock

Table 1. *Physical Properties of Base Oils*

The greases were all produced in the same reactor under similar conditions. Each grease was characterized by wt% thickener, unworked penetration, worked penetration (60x and 10,000x strokes), mechanical stability after 10,000 strokes, and US Steel mobility test. In addition, roll stability, oil separation, and dropping point were reported for some of the greases. In order to simplify the formulations, performance additives such as antioxidants, antiwear, and corrosion inhibitors were not included.

Equipment and manufacturing procedure

Manufacturing of greases not only depends upon the formulation technology, but is also greatly influenced by the processing parameters and scale up. All these samples were prepared in the laboratory at 1 to 5 gallon batch size. The kettles used for making these samples were Howard-type mixers, and controlled heat was provided through electric heating mantles. The greases based on Li 12-HSA lithium complex, clay base, and aluminum complex greases were prepared with conventional processes and compositions; varying only the base oil component. All efforts were made to keep all processing parameters, composition, and operator consistent to avoid batch-to-batch variation. The Ca sulfonate grease samples in different base oils were made in counter rotating mixers using proprietary composition and process parameters. After the greases were cooked and brought to desired penetration range, all the samples were milled through the same laboratory scale homogenization mill. The finished grease samples were tested as per ASTM standard test methods.

Discussion

Thickener Content

The amount of grease of a given consistency that may be made with a specific amount of thickening agent, i.e., grease yield, varies by thickener type and by the solvency of the oils used to prepare the grease. As the grease yield increases, the thickener content decreases, which consequently lowers the cost of the formulation since the thickener system is generally the highest priced component.

Instead of making different types of greases using a standard amount of thickener, this study did the opposite. All the greases were prepared to an NLGI Grade 2 and the amount of thickener was necessarily varied to obtain the same grease consistency. In this way, the properties of the greases could be compared on the same NLGI grade basis.

The data are plotted in Charts 1 – 4. In Chart 1, the oils are aligned in order of increasing required thickener content for the Li 12-HSA greases. This alignment, with one exception, is by type (naphthenic, paraffinic, synthetic) and by decreasing solvency as defined by increasing aniline point. The one exception is with the two ISO VG 150 naphthenics from different suppliers, where the one with the slightly higher aniline point actually requires less thickener.

Thickening efficiency is the opposite of the amount of thickener used to make an NLGI grade 2 grease. It is necessary to use a larger amount of a less efficient thickener to obtain NLGI grade 2 versus a smaller amount of a more efficient thickener. In Chart 1, the thickening efficiency of L1 12-HSA was highest for

150 N1 base oil (lowest thickener content, 10.5 wt%).

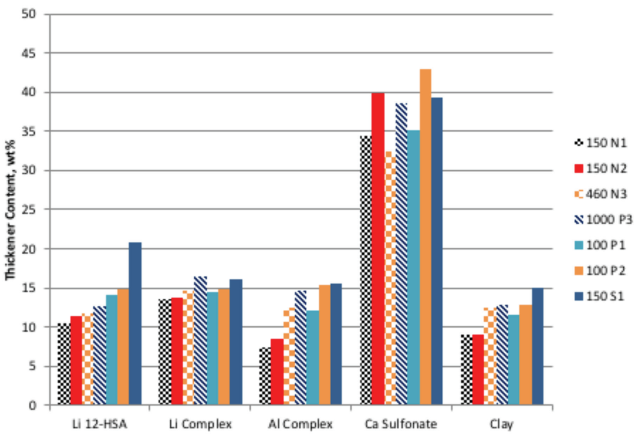

Chart 1. *Thickener Content Required for Different Greases, wt%*

For the other thickeners in Chart 1, the amounts of thickener do not always follow the same order as for Li 12-HSA. The pattern of increasing thickener content does not hold, it varies with aniline indicating that the oil to thickener interaction depends on the type and chemistry of the thickener.

For all thickener types, with the exception for the calcium sulfonate grease, the use of a naphthenic ISO VG 150 base oil reduced the amount of thickener required to formulate an NLGI Grade 2 grease. For the Li 12-HSA greases, the amount of thickener can be reduced by 25 to 30% when a naphthenic base oil is used instead of a paraffinic base oil, either a Group I or II. For the Li complex greases, the decrease in the amount of thickener was 7 to 9%. For the Al complex greases, the decrease was 40 to 50%, and for the clay greases it was 20 to 30%. For the Ca sulfonate greases, the ISO VG 460 naphthenic required slightly less thickener than the ISO VG 150 naphthenic. The decrease in the amount of thickener, compared to the paraffinic base oils, was up to 20%.

Solvency

Aromatic hydrocarbons exhibit the lowest aniline points and paraffins have the highest. The lower the aniline point, the higher or stronger the solvency of the base oil. Chart 2 plots the relationship between the aniline point of the base oil and thickener content to generate an NLGI Grade 2 grease using various thickeners. The R-squared values ranged from 0.65 to 0.97 for all thickeners except for the Ca sulfonate (R-squared = 0.09). This demonstrates the importance of the solvency of the base oil in minimizing the thickener content required to produce the target NLGI grade grease.

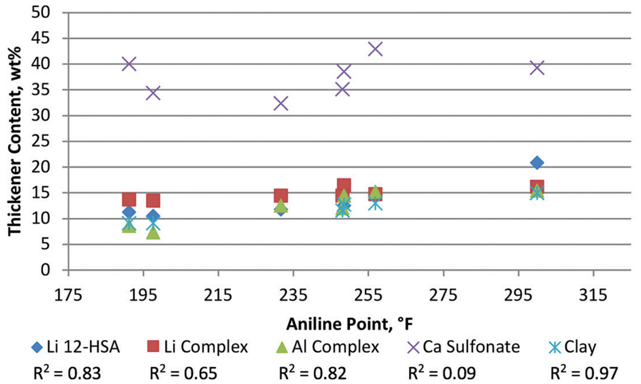

Chart 2. *Aniline Point vs Thickener Content*

In general, the higher the solvency of the base oil, the lower the required thickener content. The Ca sulfonate grease behaves differently with respect to the solvency of the base oils. Of the parameters tested, none correlated to the required calcium sulfonate thickener content.

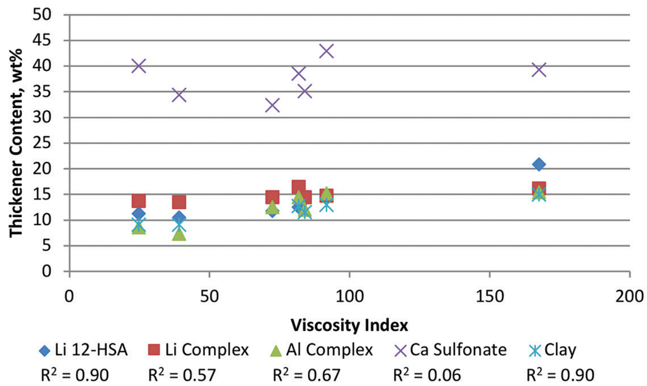

Chart 3. *Viscosity Index vs Thickener Content*

Chart 3 plots the relationship between the VI of the base oil and thickener content. Again, there are correlations (R-squared 0.57 to 0.90) between the VI of the base oil and the thickener content for all but the Ca sulfonate grease (R-squared = 0.06). The higher the VI of the base oil, the higher the required thickener content, since the VI of petroleum hydrocarbons is strongly inversely correlated with solvency.

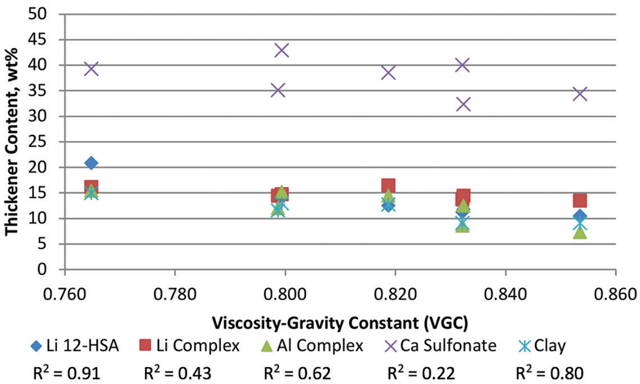

Chart 4. *Viscosity-Gravity Constant vs Thickener Content*

Chart 4 plots the relationship between the VGC and thickener content. For this parameter, there were stronger correlations and the R-squared values ranged from 0.43 to 0.91 for most greases compared to Ca sulfonate (R-squared = 0.22). Li 12-HSA had the highest R-squared at 0.91. The higher the VGC, the higher the solvency and the lower the thickener content.

Conclusions

These data have demonstrated that the solvency of the base oil is critical to the processing of the grease. The NLGI grade is defined by the penetration values which are affected by the efficiency of the thickener system, the base oil, and the thickener. By decreasing the amount of thickener to produce a particular grade of grease, the overall costs of the formulation can be reduced.

Experimental results illustrated a significant relationship between base oil solvency and thickener yield; this relationship has real economic value for grease manufacturers.

Physical properties including mechanical stability, roll stability, dropping point, oil separation, and mobility exhibited favorable results for all base oils in the study. These observations remind us that base oil selection and preference should differ according to the requirements of the application. Paraffinic chemistries maintain a leading role in engine oil applications; however, it is evident throughout our study that a specialized application, such as grease, can benefit from high solvency and low PAH content as found in modern naphthenic base oils.

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