The Effect of Polymer Additives on Grease Flow Properties

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Abstract

Grease used in centralized lubrication systems must have proper flow characteristics under operating conditions. The Lincoln ventmeter was developed as a method to determine if a particular grease is suitable for a centralized grease distribution system. The additives used in the grease may affect their suitability. A range of polymeric additives were added to lithium complex and calcium sulfonate base greases to determine their effect on grease flow properties at ambient temperatures and at -1°C. At low temperatures the effect seems to be polymer dependent. It has been shown that many types of polymers do not adversely affect the flow properties of lithium complex grease as measured by the Lincoln ventmeter. The flow properties of calcium sulfonate grease are negatively impacted by addition of polymer.

Introduction

Lubricating grease comprises two phases and three components: base fluid, thickener, and other performance additives. The liquid phase is primarily formed by the base fluid and the solid phase is formed by a network of soap molecules or a dispersion of solid particles such as inorganic clays or other fillers.[1] The solid phase thickener can consist of soap molecules with or without added polymer. The base oil solubilizes polymers and performance additives and is immobilized by the soap molecule network structure, resulting in a semi-solid to solid appearance.[2] Lubricating grease used in centralized distribution systems must have proper flow properties in order to perform efficiently and effectively. These properties are influenced by the selection of base oil, thickener and other additives.

The purpose of this paper is not to determine whether certain polymers can or cannot be used in a centralized grease distribution system but is only to examine the flow properties of a grease containing various polymer structures using the Lincoln ventmeter as a tool.

Generally, the soap thickener is a metallic salt of a long-chain fatty acid, e.g. lithium 12-hydroxy stearate, which can assemble into a network structure in solution. Polymers incorporated into the grease can be used to enhance the properties of the grease such as consistency, shear stability, water resistance, adhesion, tackiness, and soap yield.[3,4] Polymers such as polyethylene, polypropylene, polyisobutylene, halogenated polyethylene, polymethacrylate and polyurea are reported to improve the properties of greases.[1,5,6] Olefin copolymers (OCPs), styrene-ethylene-butylene (SEBS) and OCP-anhydride (OCP-A) were studied.

The type and structure of polymer selected has significant impact on grease properties including low temperature flow, thickening efficiency and shear stability.[7]

The shape of the polymer molecule is defined by its structure. Polymers with a variety of structures can be synthesized depending on the polymerization technique and catalysts used.

Figure 1 shows several polymer structures that may be obtained. Linear polymers are those with repeat units connected in a single long chain. Branched polymers or comb polymers are comprised of structures with a long backbone and multiple side chains. Star polymers and dendrimers have repeat units arranged radially.[8] The polymers studied in this paper have linear or branched structures.

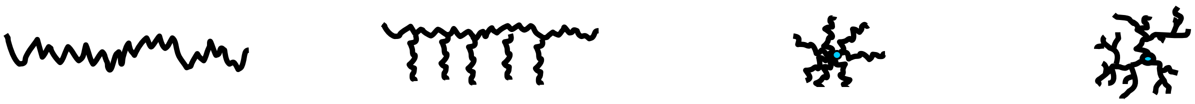

Linear Branched or Comb Star Dendrimer

Figure 1: Illustration of various polymer structures.

Base greases

The selection of the base fluid used to make the grease has a large impact on the low temperature properties. At low temperatures, paraffinic oils containing significant portions of saturated hydrocarbons generally crystallize which impedes flow.[9] Certain pour points depressants are effective at disrupting these wax crystal structures and can improve flow at low temperatures.[10]

Unlike paraffinic oils, naphthenic oils generally do not contain high levels of molecules that can crystallize at low temperature. The viscosity increase at low temperature is generally due to purely thickening effects as described by the viscosity index. Naphthenic oils are generally preferred over paraffinic oils for low temperature use.[10,11]

More recently, synthetics including polyalphaolefins and esters have been used as base fluids in greases for use at low temperature.[10,12] Similar to paraffinic oils, polyalphaolefins may contain components that crystalize at low temperature. Esters may also exhibit poor low temperature properties if, during use, cleavage of the esters into alcohols occurs.

The selection of the thickener also has an impact on the performance of grease used at low temperature. As machine design evolves operating conditions that the grease must endure has become more severe. Also, the expectation is increased machine productivity and less downtime. This has made it difficult for lithium greases to satisfactorily fulfill these requirements. The National Lubricating Grease Institute (NLGI) GC-LB specification requires greases to surpass simple lithium 12-hydroxystearate greases.

These requirements can be met by more efficient high performance greases like lithium complex, calcium sulfonate (sometimes calcium sulfonate complex), aluminum complex, polyurea and clay based greases. However, because of their compatibility with most widely used simple lithium greases, lithium complex and calcium sulfonate greases appear to be the best candidates of these high performance greases.[13] Table 1 compares the typical properties of lithium complex greases to calcium sulfonate greases.

Table 1. Comparison of typical grade 2 fully formulated greases[13]

	Lithium Complex	Calcium Sulfonate	Comments
Dropping Point	500°F	> 550°F	Higher is better
Roll Stability	8-10% change	< 5% change	Lower is better
Water Spray-off	20-60%	< 30%	Lower is better
Water Washout	5-10%	< 5%	Lower is better
EP Weld Load (kg)	250-500	> 500	Higher is better
EP Timken, (lb)	40-80	> 60	Higher is better
Wear Scar Diameter (mm)	0.5-0.6	< 0.5	Lower is better
Li Grease Compatibility	Very good	Good	

Lithium Complex vs. Calcium Sulfonate

Lithium complex greases generally possess good mechanical stability, high temperature degradation resistance and water resistance properties.[14] Other performance requirements like, antiwear, extreme pressure, rust and corrosion can further be improved by adding suitable additives. These greases, when properly formulated, meet NLGI's GC-LB specification requirements.[14]

A comparison between lithium complex and calcium sulfonate greases reveals that calcium sulfonate greases possess intrinsically better performance aspects is shown in Table 1. An important difference between these two types of greases is that calcium sulfonate greases do not typically need additives to meet certain performance requirements like lithium complex greases do. The reason for this is that the calcium sulfonate thickener in the greases is generally overbased to a high total base number (TBN). The active chemistry in addition to the calcium sulfonate matrix is amorphous, oil soluble calcium carbonate.[15]

Other benefits of calcium sulfonate greases include superior mechanical and roll stability compared to lithium complex greases. This can be attributed to lower leakage and run out during operation. These greases also have higher dropping points and may be used at higher temperatures than lithium complex greases.[15]

Calcium sulfonate thickeners have inherent extreme pressure, antiwear properties and are known to be natural rust inhibitors. Many of these thickeners provide excellent water-resistance and do not break down in the presence of water. Lithium complex greases usually require tackifiers to improve their water-resistance properties.[15]

Calcium sulfonate greases are also compatible with lithium and lithium complex greases. However, calcium sulfonate greases suffer from inferior pumpability and high cost when compared to lithium complex greases.[13]

Grease Flow

Grease flow is a complex phenomenon determined by many factors. The most important factor is temperature. As the temperature decreases a grease will have poorer mobility. Other factors include thickener type and amount, base oil properties and other mobility improvers.

The most readily pumpable or dispensable greases are made from lithium complex or aluminum complex soaps. Less readily pumpable greases are based on calcium complex and calcium sulfonate type soaps. Calcium sulfonate greases contain a higher level of soap to attain a particular NLGI grade compared to lithium complex greases. This accounts for the decreased flow rate of calcium sulfonate greases.

The base oil accounts for 80 to 90% of a typical grease. Therefore, its properties strongly influence grease flow. High viscosity base oils result in lower mobility greases; however, in machinery operation these greases provide better lubricity through increased film thickness. Base oils with low viscosity indexes generally have poorer mobility at lower temperatures. Higher base oil pour points indicate the presence of waxy components, which restrict mobility as they crystallize at low temperature.

Mobility improvers are generally low pour point, low viscosity oils or solvents. These can include synthetic esters and polyalphaolefins.[16]

Current Test Methods

A property that is often associated with low temperature performance is the consistency of the grease. There are several methods used to attempt to adequately describe the consistency and flow characteristics of the grease. The NLGI grade of a grease as measured by cone penetration (ASTM D217) is a simple method of numerically describing the consistency of a particular grease at a given temperature.[17] Cone penetration values at one temperature have not been shown to be particularly good predictors of values at another temperature or indication of flow properties at low temperatures.

The apparent viscosity of a grease may also be determined using a rheometer, commonly set up as a plate-plate system.[10] The amount of torque required to turn one plate may be recorded at several temperatures. An increase in the torque required implies that the grease has a higher viscosity and will therefore flow less well. A series of capillary rheometer runs can also be used such as in the ASTM D1092 Apparent Viscosity test.[18,19]

The two tests most frequently used to determine the pumpability or dispensability of a lubricant are the U.S. Steel mobility test and the Lincoln ventmeter test.

The U.S. Steel mobility test determines the resistance of lubricating grease to flow at a given temperature and pressure. Mobility is determined by the flow rate of the grease through a pressure viscometer.[20] Typically the pressure viscometer is constructed of stainless steel and is fitted with a No. 1 (40:1 ratio) capillary. With the sample at the test temperature, the flow of grease is started under the selected pressure using a nitrogen tank and regulator. Typical test pressure is 150 psi and temperatures of ambient, 32°F, 20°F, 10°F, and 0°F. Flow rate, usually measured in grams per second, is determined by collecting the grease for a specified period.

The ventmeter test was developed by Lincoln St. Louis to evaluate the compatibility of different greases with their SL-1 and SL-11 injector systems at various temperatures.[21] Today, it is primarily used to evaluate the low temperature flow performance of a grease in a centralized lubrication system.

The ventmeter contains 25 feet of coiled $^1/_4$ inch diameter steel tubing. Inlet (valve #1) and outlet (valve #2) valves are attached at each end of the coiled tubing.[19,21] Figure 2 shows the internal design of the ventmeter. The data collected with the apparatus can be used to calculate an approximate yield stress.[22] This parameter is important in the design of a centralized lubrication system.[19]

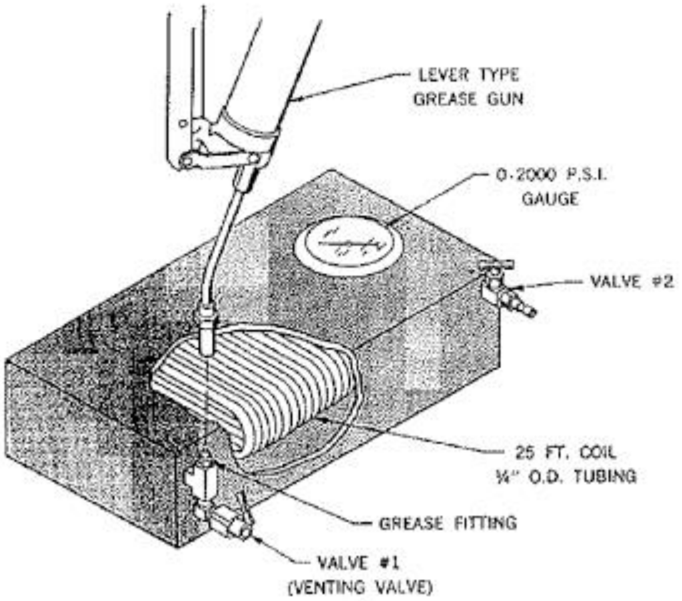


Figure 2: Schematic of the Lincoln ventmeter.[21]

A standard grease gun is filled with test grease and is attached to the ventmeter through a hydraulic grease fitting. The ventmeter is then filled with grease by pumping the grease gun handle. All air is expelled in the charging process.[19]

A pressure gauge is located at the outlet side of the ventmeter Valves 1 and 2 are both closed and additional grease is pumped into the instrument to develop a pressure of 1800 psi. Valve 1 is opened for 30 seconds and the vent pressure is recorded. To measure grease flow at temperatures other than ambient, the filled ventmeter and grease gun assembly are placed into a freezer and allowed to equilibrate to the test temperature for a minimum of 3½ hours.

Materials

The base greases used were a Lithium Complex Grade #2 grease containing 10% soap without any additional additives and a calcium sulfonate base grease containing 26% of 400 TBN calcium sulfonate. The base oil viscosity was 73 cSt at 40°C, and was a blend of 100N and 500N Paraffinic Group I base oils.

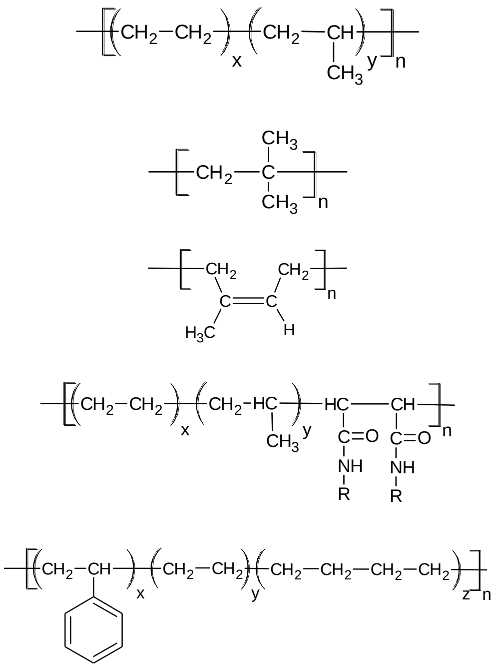
Ethylene-propylene copolymer (OCP, OCP-L)

Polyisobutylene (PIB)

Polyisoprene (PIP)

Ethylene/propylene copolymer grafted with anhydride/acid/ or amide (OCP-A, OCP-P, OCP-M)

Styrene-ethylene-butylene copolymer (SEBS)



Modified poly(butene-1) (PB) Proprietary

Figure 3: Types of polymers used in this study, their abbreviations and structures.

Polymers were incorporated into the base grease by mixing in a Hobart mixer at 80°C. The polymer additives used in this study were in powder, liquid or pellet form and are shown above in Figure 3. Polymers were added and mixed for 3 hours to ensure complete solubilization of the polymer. For reference, the base grease was heated and stirred using the same process as the samples containing the powdered polymers.

Experimental Methods

A Lincoln ventmeter was used to determine the flow properties of greases. A manual grease pump was bulk-loaded and used to fill the ventmeter. After filling the ventmeter the outlet valve was closed and pressure was applied using the grease pump up to 1800 psi. The test valve was then opened for thirty seconds and the pressure was recorded. The final pressure reading was recorded from these values. Final pressure values were normalized to an initial pressure of 1800 psi to account for small variations between runs. Measurements were performed at ambient temperature and -1°C (30°F).

Results and Discussion

Lithium Complex Greases

At ambient temperature there are no significant differences in the final ventmeter pressure reading of the greases when compared to each other or the base grease, as shown in Figure 4. This indicates that adding polymer to improve other characteristics of the grease such as water spray-off or grease consistency does not have an impact on the flow properties of these greases.

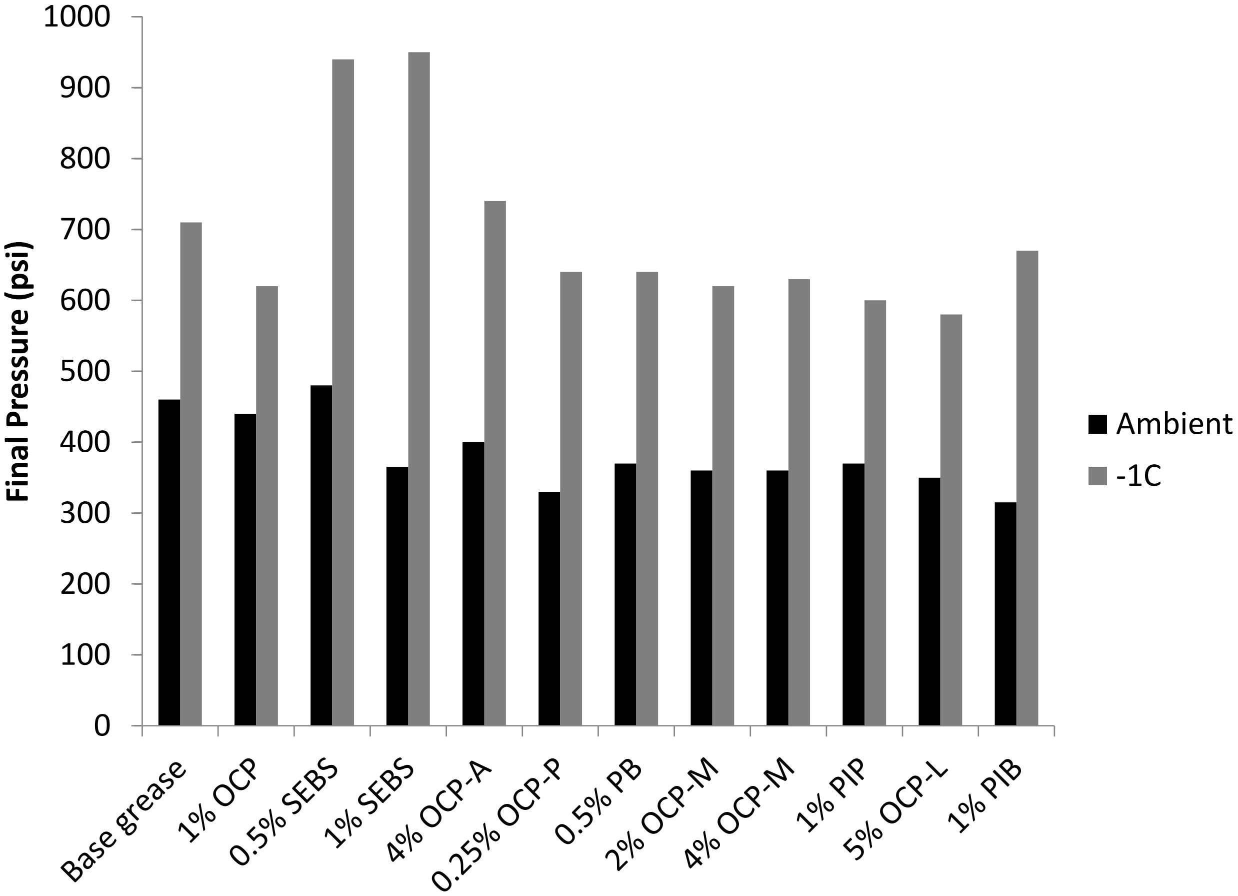


Figure 4**:** The final pressure recorded using the Lincoln ventmeter in lithium complex greases. An increase in final pressure represents a grease that flows less well.

At -1°C, there are generally no significant differences in the final pressures recorded when compared to each other or the base grease, as shown above in Figure 4. However, greases containing 0.5 or 1 wt% of SEBS show a significant increase in final pressure reading. This increase corresponds to decreased flow at -1°C. SEBS has a negative impact on flow at low temperature when used in this lithium complex base grease. This may be due to the styrene content of this polymer additive. At low temperatures the styrene is less soluble and can form large domains of styrene. These domains can aggregate and result in the formation of a strong network that will resist flow. As a result of this strong network, the SEBS forms the stiffest greases measured by cone penetration measurements. Decreasing the temperature will drive more styrene into these domains further increasing the strength of the network and thus the stiffness of the grease.

The grease flow as measured with the ventmeter at ambient temperature or -1°C does not seem to show any dependence on the stiffness of the grease as measured using cone penetration, as shown in Figure 5. There is also no dependence on the water spray-off values, as shown in Figure 6. No correlation between water spray-off and flow properties would be expected.

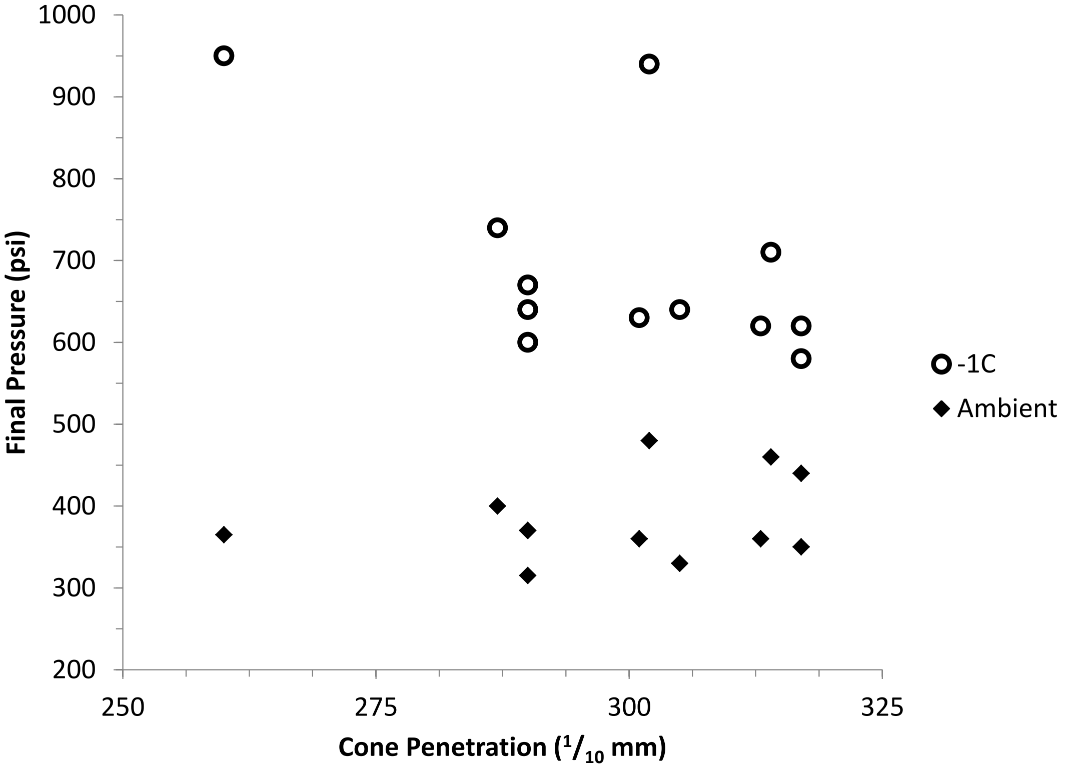


Figure 5: The final pressure in lithium complex greases shows no dependence on the cone penetration at either temperature studied.

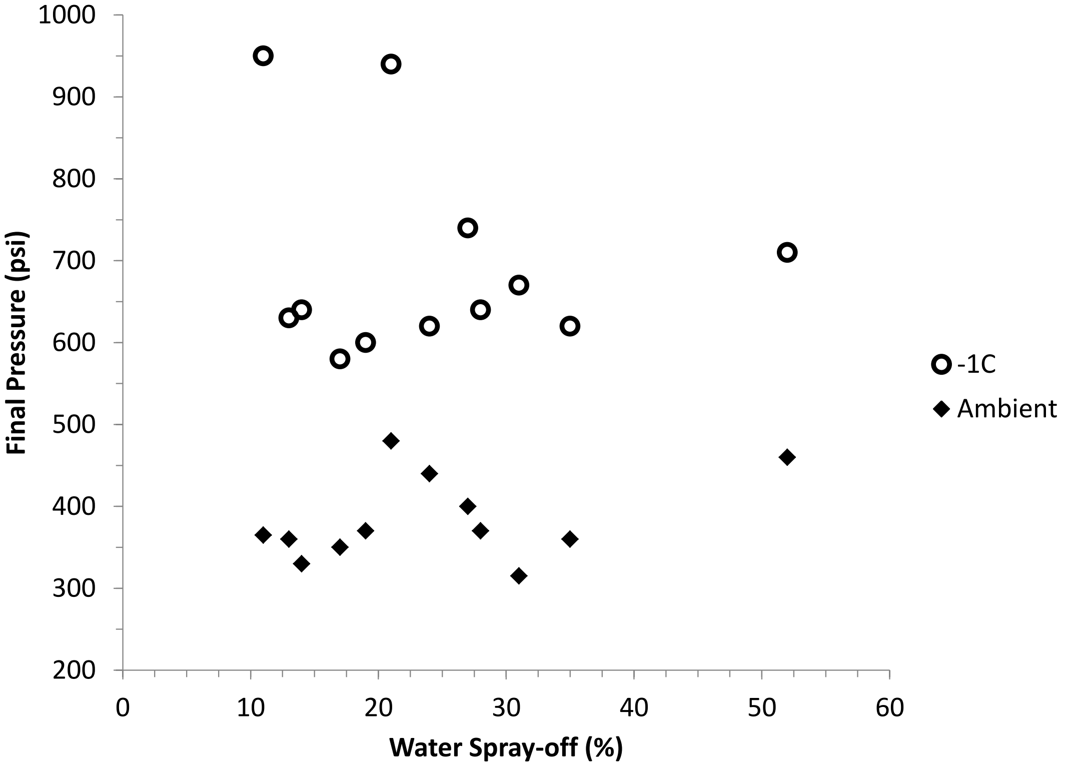


Figure 6: The final pressure in lithium complex shows no dependence on water spray-off values at either temperature studied.

Calcium Sulfonate Greases

In the case of calcium sulfonate greases, adding polymer significantly decreases flow at both ambient temperature and -1°C when compared to the base grease, as shown in Figure 7. Unlike the case of lithium complex greases, there is little significant difference in flow properties when the type of polymer is taken into consideration. The final ventmeter pressure reading is similar for each type of polymer included. It seems that the addition of any additional network to the grease is enough to substantially impact flow regardless of how relatively weak or strong the polymer network is.

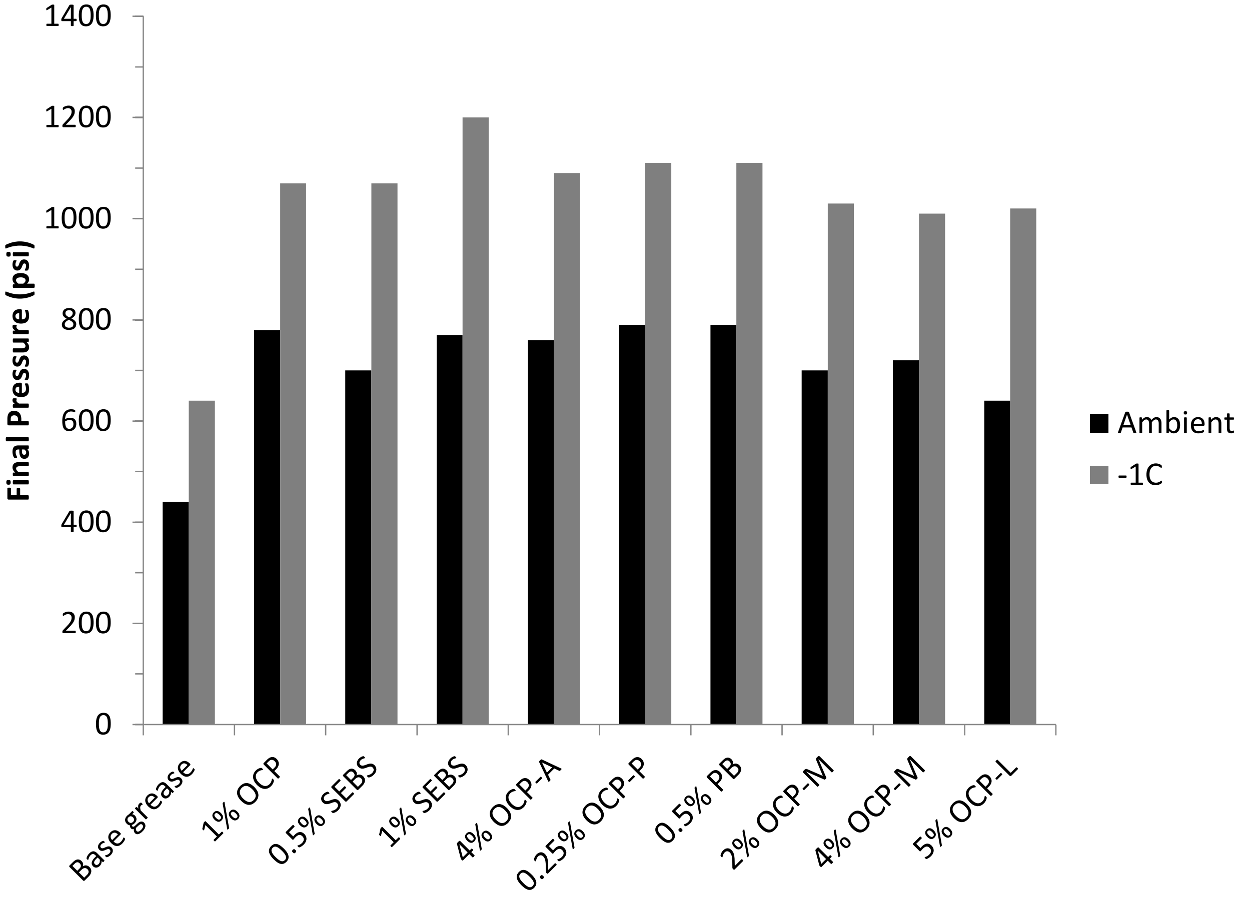


Figure 7: The final pressure ventmeter readings for calcium sulfonate greases. A higher final pressure indicates a grease that flows less well.

As in the case of lithium complex grease, there does not seem to be a dependence of flow properties on either the cone penetration or the water spray off values, as shown in Figure 8 and Figure 9, respectively. The base grease is clearly shown to have a lower final pressure than those greases containing polymer.

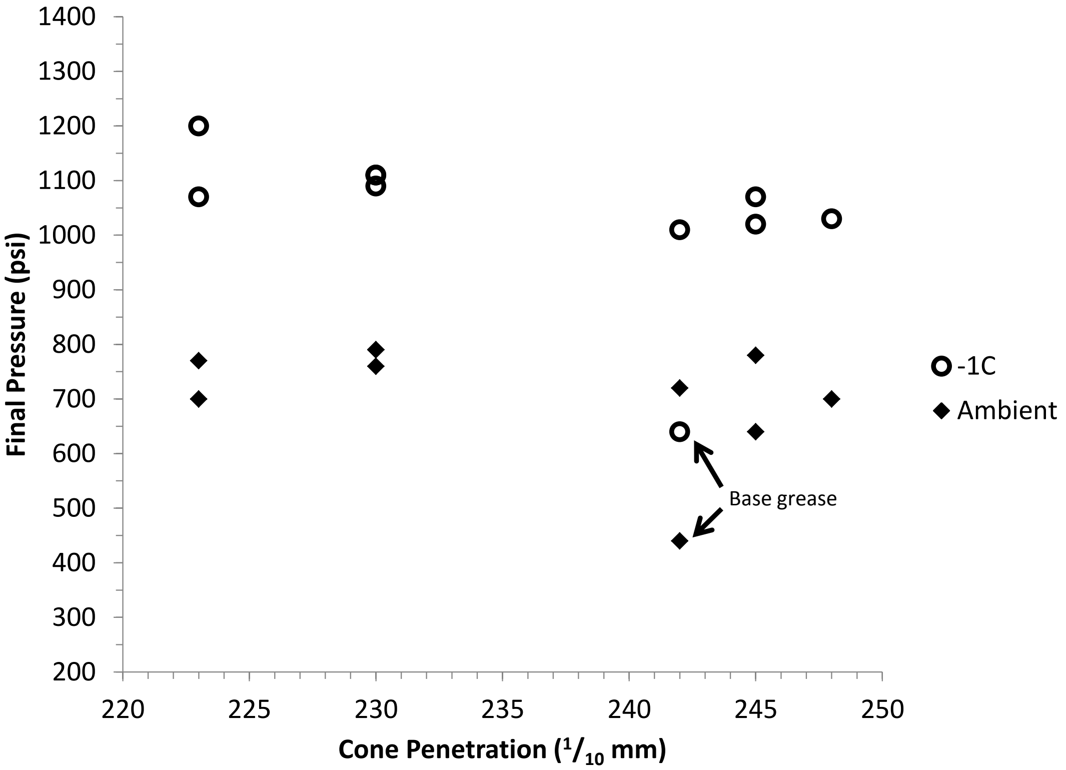


Figure 8: The final pressure in calcium sulfonate greases does not depend on the cone penetration at either temperature studied.

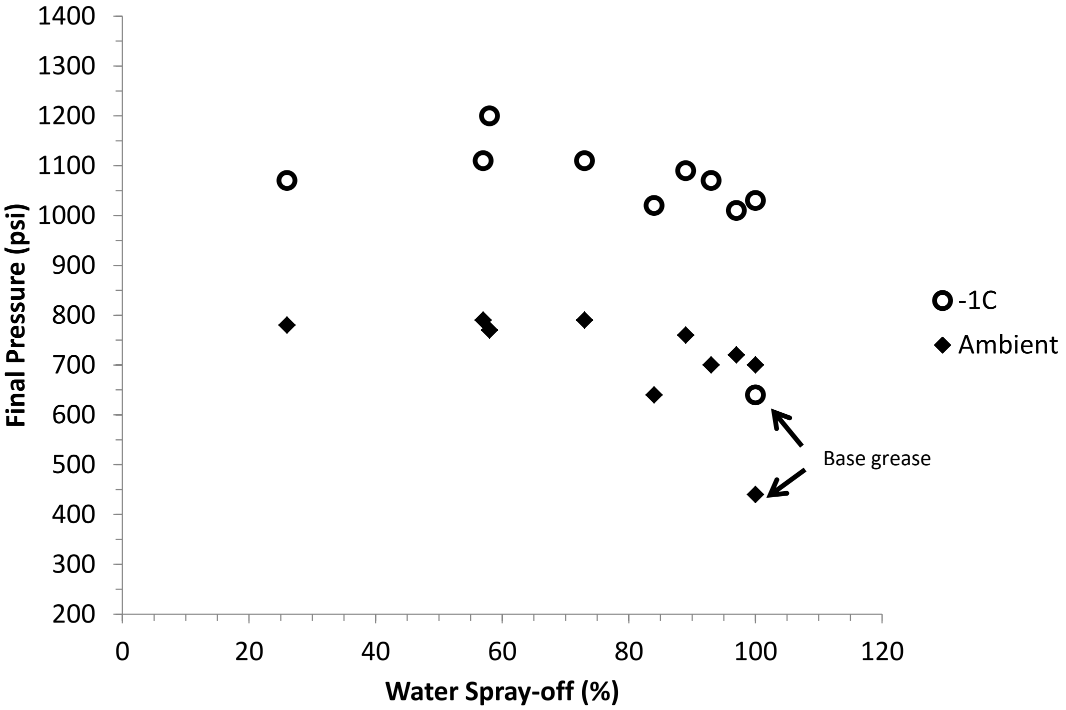


Figure 9: The final pressure in calcium sulfonate greases does not depend on the water spray-off values at either temperature studied.

Conclusion

Adding polymer to grease does not affect lithium complex grease flow at ambient temperature or -1°C as compared to the base grease without polymer, with the exception of the styrene containing SEBS which forms a relatively stiff network at -1°C and adversely affects flow. Adding 4% OCP-M to a lithium complex base grease represents the best compromise between water spray-off performance and low temperature flow properties.

Any polymer significantly decreases flow in calcium sulfonate greases. If a polymer must be added, selecting 1% OCP to a calcium sulfonate base grease seems to be the best compromise between good water spray-off and flow properties. These issues may be overcome using pour point depressants or other mobility improvers in fully formulated low temperature greases.

A similar study could be performed using aluminum complex and clay thickened greases containing various polymer additives.

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Appendix

Lithium Complex Grease Data

			Ventmeter Conditions					
	Cone Penetration ($^1/_{10}$ mm)	**Water Spray-off (%)**	**Temperature**	**Initial Pressure (psi)**	**Final Pressure (psi)**	**Pressure Drop (psi)**	**Normalized Final Pressure (psi)**	**Ambient Temperature**
Base grease	314	52	Ambient	1800	460	1340	**460**	24.0°C
			-1°C	1790	700	1090	**710**	
1% OCP	317	24	Ambient	1760	400	1360	**440**	24.0°C
			-1°C	1820	640	1180	**620**	
0.5% SEBS	302	21	Ambient	1780	460	1320	**480**	26.5°C
			-1°C	1800	940	860	**940**	
1% SEBS	260	11	Ambient	1860	425	1435	**365**	27.0°C
			-1°C	1800	950	850	**950**	
4% OCP-A	287	27	Ambient	1800	400	1400	**400**	27.5°C
			-1°C	1780	720	1060	**740**	
0.25% OCP-P	305	14	Ambient	1800	330	1470	**330**	27.5°C
			-1°C	1820	660	1160	**640**	
0.5% PB	290	28	Ambient	1800	370	1430	**370**	24.0°C
			-1°C	1800	640	1160	**640**	
2% OCP-M	313	35	Ambient	1800	360	1440	**360**	26.0°C
			-1°C	1800	620	1180	**620**	
4% OCP-M	301	13	Ambient	1800	360	1440	**360**	25.5°C
			-1°C	1820	650	1170	**630**	
1% PIP	290	19	Ambient	1800	370	1430	**370**	23.0°C
			-1°C	1800	600	1200	**600**	
5% OCP-L	317	17	Ambient	1800	350	1450	**350**	23.5°C
			-1°C	1820	600	1220	**580**	
1% PIB	290	31	Ambient	1800	315	1485	**315**	23.0°C
			-1°C	1780	650	1130	**670**	

Calcium Sulfonate Grease Data

			Ventmeter Conditions					
	Cone Penetration ($^{1}/_{10}$ mm)	**Water Spray-off (%)**	**Temperature**	**Initial Pressure (psi)**	**Final Pressure (psi)**	**Pressure Drop (psi)**	**Normalized Final Pressure (psi)**	**Ambient Temperature**
Base grease	242	100	Ambient	1800	440	1360	**440**	23.0°C
			-1°C	1820	660	1160	**640**	
1% OCP	245	26	Ambient	1810	790	1020	**780**	25.0°C
			-1°C	1810	1080	730	**1070**	
0.5% SEBS	223	93	Ambient	1840	740	1100	**700**	26.5°C
			-1°C	1800	1070	730	**1070**	
1% SEBS	223	58	Ambient	1810	780	1030	**770**	25.5°C
			-1°C	1810	1210	600	**1200**	
4% OCP-A	230	89	Ambient	1800	760	1040	**760**	23.0°C
			-1°C	1800	1090	710	**1090**	
0.25% OCP-P	230	57	Ambient	1800	790	1010	**790**	24.0°C
			-1°C	1800	1110	690	**1110**	
0.5% PB	230	73	Ambient	1800	790	1010	**790**	23.5°C
			-1°C	1800	1110	690	**1110**	
2% OCP-M	248	100	Ambient	1840	740	1100	**700**	24.5°C
			-1°C	1810	1040	770	**760**	
4% OCP-M	242	97	Ambient	1790	710	1080	**720**	24.5°C
			-1°C	1790	1000	790	**1010**	
5% OCP-L	245	84	Ambient	1800	640	1160	**640**	26.0°C
			-1°C	1800	1020	780	**1020**	