

Shear Improvement: Polymers Keep Mechanical Stability

BY ERIK WILLETT

Polymers have long been used to tailor the properties of lubricants and greases. Grease polymers in particular uniquely benefit grease in the areas of mechanical stability, water resistance, yield and tackiness.

Grease polymers can have an effect on cone penetration test results and consistency of grease. Thickening from the grease polymer translates to added yield per weight of thickener and is often used to improve the economics of grease products.

However, the use of high molecular weight polymers to add consistency in grease often requires accounting for the effect of mechanical shearing on the polymer. Large molecules like polymers are subject to higher stresses and strains, which can result in mechanical breakdown of the grease and lead to equip-



ment damage or failure. Grease polymer manufacturer Functional Products designed a study to address two fundamental questions:

1. Do grease polymers contribute to grease consistency and NLGI grade?

2. If so, can the consistency added by the polymer withstand mechanical shearing by a test method such as ASTM D1831 roll stability test? The researchers were surprised to find that the majori-

ty of greases with increased consistency due to the addition of polymers showed no change in mechanical stability, and nearly a quarter actually showed an increase in ability to withstand shear.

Grease Polymers 101

Grease polymers act by modifying the structure of grease and changing how individual molecules or fibers of thickener associate. Normally, grease is held together by several types of short-range interactions, including hydrogen



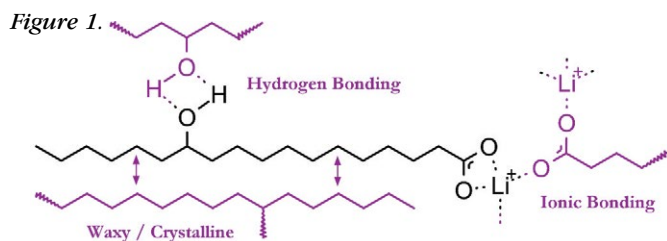
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bonding and waxy and ionic bonds. (See Figure 1.) These non-covalent bonds, which do not share electrons, have varying strength and effects on grease stability. For example, consider the melting points of stearyl alcohol (60 degrees Celsius), C18 alkane (30 C) and lithium stearate (220 C)—a higher melting point indicates a stronger bond.

Grease polymers are chosen based on their ability to form a second network that is complementary to the grease thickener network. A good metaphor for this relationship is the way that rebar is used to strengthen concrete.

Grease polymers, like rebar, form flexible networks over long ranges due to many carbon-carbon bonds in the polymers. These exist inside of the inorganic grease structure, which, like concrete, is tough but brittle due its short-range, non-covalent bonds.

When polymer is added to grease, the polymer network and the thickener network merge to form an interpenetrating network. Temperatures of 80 to 120 C, which are far below dropping point, are typically used in this stage of grease making. The polymer is added in liquid or solid form and mixed



until homogeneous. The thickener and polymer networks reform as the grease cools and rests.

Three main mechanisms ensure the polymer network forms and remains locked around the grease network. These mechanisms are related to the three short-range interactions that hold grease together as shown in Figure 1.

- **Temperature Sensitivity.** Long, uninterrupted runs of one monomer (e.g. ethylene or styrene) along the backbone of the polymer form waxy crystallites between chains. This bond can be compared to Velcro tape.
- **Hydrogen Bonding.** Polar nitrogen and oxygen sites on the polymer separate from the non-polar oil and associate together in an acid-base attraction, somewhat like magnets.
- **Reactivity.** Acid anhydride sites on the polymer react with metal ions to form insoluble coordination complexes, like diacids, or react with hydroxide

sites to form covalent bonds in the thickener, like boron esters. This bond can be compared to glue.

Tackifiers—very high molecular weight polymers used to impart stringiness and cohesion to oil and grease—may also provide an additional mechanism through the formation of physically entangled chains that bind together the thickener network over very long ranges. Tackifiers do not form the types of short-range attractions listed above, but often do provide some of the benefits of grease polymers through that entanglement.

Grappling with Grease Grades

In order to determine whether polymers affect grease grade, six NLGI grade 2 base greases were obtained from commercial sources: simple lithium, lithium complex, calcium sulfonate, aluminum complex, silica and bentonite clay. All greases were prepared with typical

Three short-range interactions of various strengths hold a thickener network together in lithium 12-hydroxystearate grease.

industrial grease additives for multi-purpose use—minus any grease polymers—and milled. Each grease used high-viscosity ISO 100 to 460 API Group II base oil.

A total of nine polymers were added individually to the six greases. Two polymers each, a low molecular weight (100,000-200,000 grams per mole) and a high molecular weight (300,000-600,000 g/mol) version, were selected from each of the three categories of interpenetrating network formation described above. Performance of the polymer varies based on the number and ratio of the monomers, the molecular weight, crystallinity and other structural factors.

A lower molecular weight olefin copolymer tackifier and very high molecular weight polyisobutylene tackifier were also included to see the effects of an entangled polymer network. A dispersant polymethacrylate was added to the study as a third “hydrogen bonding” polymer but also to see the extent of inter-

Table 1. NLGI Grade of Modified Greases vs. Controls

	Simple Lithium	Lithium Complex	Calcium Sulfonate	Aluminum Complex	Silica	Bentonite Clay
Control (5% oil, no polymer)	1.5	2	2.5	2.5	1	0
V-207 Temp. Sens. Polymer (Low MW)	2	3	2.5	2	2	0
V-4064 Temp. Sens. Polymer (High MW)	2	2.5	2.5	2.5	1	0
V-508S H-Bonding Polymer (Low MW)	1.5	2.5	2.5	1.5	1	0.5
V-191 H-Bonding Polymer (High MW)	2.5	2.5	3	3	2	1
V-4033 Reactive Polymer (Low MW)	2	3	3	2.5	1	0.5
V-4020 Reactive Polymer (High MW)	2	2	2	3	1	0.5
V-188 Tackifier (Low MW)	2	2.5	3	2	2	0
V-175F Tackifier (High MW)	2	2	3	2.5	1	0.5
MD-9000 Dispersant PMA (High MW)	2	2	2	2.5	1	0

Analytics: No change: 21 greases (39%), +0.5: 21 greases (39%), +1: 7 greases (13%), -0.5: 4 greases (7%), -1: 1 grease (2%)

action with a polymethacrylate.

Each polymer was prepared as a solution of 8 to 10 weight percent polymer in 100 neutral paraffinic oil before adding 5 wt% solution to 95 wt% base grease to deliver a final polymer concentration of approximately 0.45 wt%. Polymers were pre-dissolved to allow efficient and reproducible incorporation of the polymer into the many different grease systems in this study.

In all, 54 greases were prepared in order to observe how different combinations of greases and polymers influence NLGI grade. Samples where polymer increased the NLGI grade by 0.5 or more were later used in the roll stability test in the second half of the study.

Table 1 summarizes the changes in NLGI grade with the addition of polymers versus simply adding the diluent oil without polymer (the control). Of the 54 samples, 21 samples experienced no change in NLGI grade after adding 5 wt% liquid polymer versus the control of 5 wt% pure 100 N diluent oil. Half of the greases resulted in a half or full increase in NLGI grade. Five samples lost NLGI grade by a half or full grade. Half

grades are consistencies that fall within the gap of cone penetrations between two grades.

Gauging Grease Stability

Why NLGI grade increases is a separate discussion, but more often than not, grease polymers increase NLGI grade and the consistency of grease. Grease polymers that add consistency would be at risk of mechanical shearing because of their molecular length, so further work was carried out to measure the stability of grease with high consistency increase.

Twenty-seven polymer-modified grease samples showing an increase in consistency were tested and compared against the roll stability changes of the control greases. Table 2 summarizes the changes to consistency after the ASTM D1831 roll stability test, with positive values meaning a loss of consistency (thinning) and negative values meaning an increase in consistency (thickening).

Cone penetration before and after roll stability was assessed with quarter-cone measurement, which yields an estimated 3.8 percent relative error by ASTM D1831. Changes, positive or negative, within this error were

deemed negligibly different.

Of the 27 samples, 15 demonstrated negligible changes to roll stability versus the control. Simple lithium and clay greases were improved by up to a full NLGI grade using polymer without an effect on shear stability. Six samples showed statistically relevant improvement in shear stability outside ASTM D1831 error.

In total, 78 percent of cases of polymer-modified grease with increased NLGI grade from polymer yielded either no change or a positive change in roll stability. Globular or micellar structured greases like calcium sulfonate and aluminum complex were the most sensitive to consistency gains from polymer, with many modified greases of these types demonstrating a loss of mechanical stability in roll stability testing.

For nine polymers in six greases, it was demonstrated that grease polymers are typically neutral or positive toward increasing consistency and NLGI grade. This may happen intentionally as part of increasing thickener yield or as a byproduct of improving tackiness, water resistance or oil bleed.

When NLGI grade was

increased, roll stability was generally not negatively affected, with 56 percent of tested cases showing no appreciable change in ASTM D1831 roll stability and 22 percent showing an increase in mechanical stability.

The results of this study are intended as a starting point for formulators and are not a definitive guide. Most greases, even of the same kind, will vary widely by factors such as the thickener used, the base oil, NLGI grade and production method. ■



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Table 2. Change in Cone Penetration after Roll Stability Testing

	Simple Lithium	Lithium Complex	Calcium Sulfonate	Aluminum Complex	Silica	Bentonite Clay
	+1.2%	+36.1%	+3.1%	+1.5%	+2.3%	+11.3%
V-207		+21.5%			(+2.6%)	
V-4064	(+1.5%)	+19.8%				
V-508S		(+37.9%)				(+11.5%)
V-191	(+1.5%)	+25.6%	+11.7%	+18.9%	+7.9%	(+9.4%)
V-4033	(-2.6%)	+22.5%	+9.8%	-5.2%		
V-4020	(+0.0%)			+14.5%		(+12.5%)
V-188		+17.8%	(+4.6%)		+2.6%	
V-175F	(-2.1%)		(+1.6%)			(+13.8%)
MD-9000	+6.6%					(+8.6%)

Blank entries were not tested. Entries in parentheses indicate no significant change compared to the control. Bold entries indicate improved roll stability (lower percent change). Purple entries indicate worse roll stability (higher percent change). **Analytics:** Same: 15 greases (56%), More stable: 6 greases (22%), Less stable: 6 greases (22%)