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Additives for lubricating grease

A skillfully formulated grease brings a host of good things.

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KEY CONCEPTS

- Grease is a liquid lubricant that's been solidified to keep it in the intended location.
- Applications determine the exact additive requirements of a lubricating grease.
- Lubricant additives are molecules consisting of a polar head, a linking group and an oil-soluble tail and can be divided into two groups: physical and chemical.

JUST AS LUBRICATING OILS REQUIRE VARIOUS PERFORMANCE ADDITIVES IN KEEPING WITH THEIR INTENDED USES, SO DO LUBRICATING GREASES CONTAIN ADDITIVES selected to ensure that they satisfy the customer's expectation of long life and effective protection of metal parts from the ravages of friction and corrosion.

The information in this article derives from an STLE Webinar titled "Performance Additives for Lubricating Grease" presented May 7, 2014, by Dr. Gareth Fish, technical fellow in the Industrial Additives Division at The Lubrizol Corp. in Wickliffe, Ohio.

Grease is a liquid lubricant that's been solidified to prevent it from escaping the location needing protection. A handy way to remember that is base oil + thickener + additives = grease. Lubricating grease typically contains about 50%-95% base oil stock, combined with 3%-45% thickener and 2%-8% additives. The relatively small volume that additives occupy in grease is a reminder of the power these compounds and complexes impart to a recipe for a lubricating grease.

A skillfully formulated grease can bring to the user a host of good things. These include consistency, oxidative and thermal sta-

MEET THE PRESENTER

This article is based on a Webinar originally presented by STLE University. "Performance Additives for Lubricating Greases" is available at **www.stle.org**: $39 to STLE members, $59 for all others.

Dr. Gareth Fish received a bachelor's of science degree in chemistry in 1984 and a doctorate degree in tribology in 1990 from Imperial College of Science, Technology and Medicine in London. From 1988-1990 he worked at the UK Ministry of Defence, Fuels and Lubricants Branch, the Royal Arsenal in Woolwich, England, working on military lubricants and greases. In 1990 he worked as a tribologist on automotive transmission components and greases for GKN Technology Ltd. in Wolverhampton, England. In 2002 he was in charge of tribology, lubricants and sealing materials testing at GKN Automotive, Inc., in Auburn Hills, Mich. In 2007 he worked as a grease technology manager for The Lubrizol Corp. and currently works there as technical fellow in the Industrial Additives Division.

Dr. Fish is a member of the Royal Society of Chemistry, the Energy Institute, STLE, ASTM and SAE. He is the chair of ASTM D02.G07 Grease Research Techniques and D02.B04 Automotive Greases. He was the 2013-2014 chair of the STLE CLS Committee.

He is a Chartered Scientist, an STLE Certified Lubrication Specialist™ and an NLGI Certified Lubricating Grease Specialist. He has authored more than 40 technical papers on grease and tribology and three book chapters. He holds three U.S. patents and is the winner of two NLGI Clarence E. Earle Memorial Awards. Dr. Fish also received an NLGI Authors Award and the Chevron Prize for grease publications. He was the winner of the NLGI Fellows Award and the NLGI SOPUS prize for teaching excellence. He won the Best Paper Award in 2015 at the ELGI Annual Meeting in Barcelona. You can reach Gareth at **gareth.fish@Lubrizol.com**.

Dr. Gareth Fish

bility, corrosion resistance, structural stability, load-carrying capability, wear protection, low-temperature performance, high dropping point and elastomer compatibility.

Applications determine the exact additive requirements of a lubricating grease. For example, are the metal parts needing lubrication moving quickly or slowly? Are they working under high mechanical loads or low ones? These factors can determine the needed viscosity. If parts spend a lot of time standing still or frequently reverse the direction in which they move, an additive may be called for to prevent fretting of metal surfaces. When a grease is expected to tolerate high-working temperatures it may need an increased amount of antioxidant additive. Other considerations can include the odor of a lubricant product. How does it smell? Are there disposability or environmental factors affecting a product? How do the price tags of competing lubricants compare? All of these requirements dictate the types of additives needed in the grease for that application.

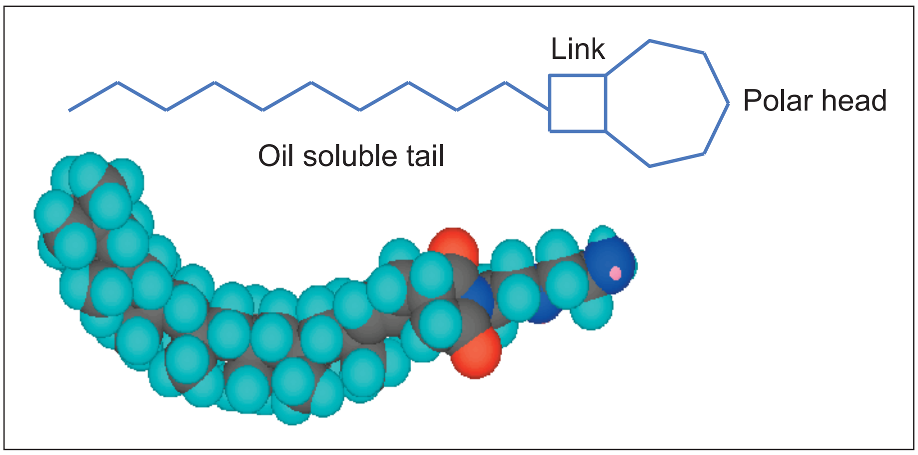

Figure 1 | **An additive molecule consisting of a polar head, linking group and oil-soluble tail.** (*Courtesy of The Lubrizol Corp.)*

Lubricant additives are typically molecules consisting of a polar head, a linking group and an oil-soluble tail consisting of 8-22 carbon atoms (*see Figure 1*). They can be divided into two groups: physical and chemical. Physical additives undergo no chemical reactions but affect the physical properties of the grease. These can include structure and rheology, the tendency of oil to bleed out of the grease and water tolerance. Chemically active additives can be one of two types. The first type reacts at the contacting surfaces of metal parts, working to inhibit corrosion, impart extreme pressure tolerance or provide antiwear properties. The second type reacts within the matrix of the grease and serves as antioxidants or structure modifiers.

Widely used additives include solid lubricants and dyes. There are about 25 solid additives in use including molybdenum disulfide, graphite and powdered PTFE, to name just a few. These substances form easily sheared structural planes that slide against each other like playing cards in a deck (*see Figure 2*). They protect heavily loaded bearings from fretting wear, scuffing and seizing and can fill in local surface irregularities on metal parts.

Inhibiting oxidation is one of the most important functions performed by additives. The chemical bonds in a hydrocarbon such as the base oil can be broken by heat and by finely divided metallic wear particles. These broken bonds known as radicals will react with oxygen to form unstable intermediates that either decompose or form more broken bonds, and the reaction continues. When the reaction follows the path of oxidation, it produces undesirable degraded products such as varnishes, lacquers and gums (*see Figure 3*). Such reaction products can prevent bearings from rotating smoothly and cause them to fail. Under these circumstances, the grease may stiffen up, crack, lose structural integrity, increase in acidity and show a fall in dropping point. They are all unwanted effects of grease oxidation. The worst case scenario is that the grease fails, a bearing seizes and brings machinery to a screeching and costly halt.

Oxidation inhibitors come to the rescue and stop this chain of events by scavenging and mopping up the radicals that have formed in the grease. Metal dithiophosphates, hindered (alkylated) phenols and aromatic amines are used for this purpose. When they are added to grease, 0.5% substituted phenol plus 0.5% arylamine have a synergistic effect yielding better oxidation reduction than the components alone would yield when used at the same overall treat rate. Oxidation resistance of the combined additives is substantially enhanced from the sum of the constituents. This formula is often used in high-temperature grease (*see Figure 4*).

Corrosion and rust inhibitors work by one of two different mechanisms. "Offensive protection" is provided by acid neutralizers, additives that neutralize aggressive acid products and render them innocuous. "Defensive

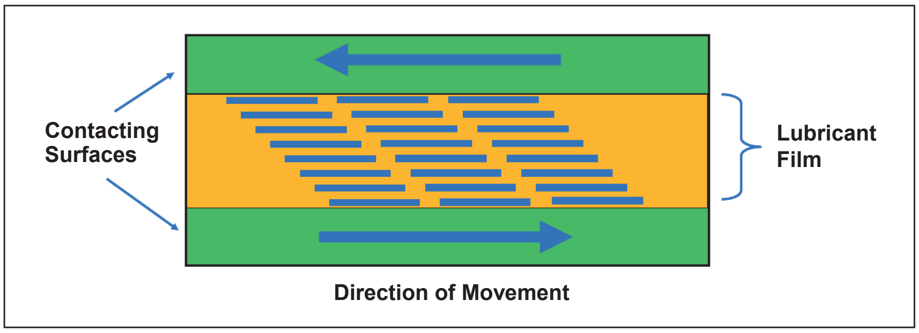

Figure 2 | **A solid additive mechanism forms easily sheared structural planes that slide against each other like playing cards in a deck.** (*Courtesy of The Lubrizol Corp.*)

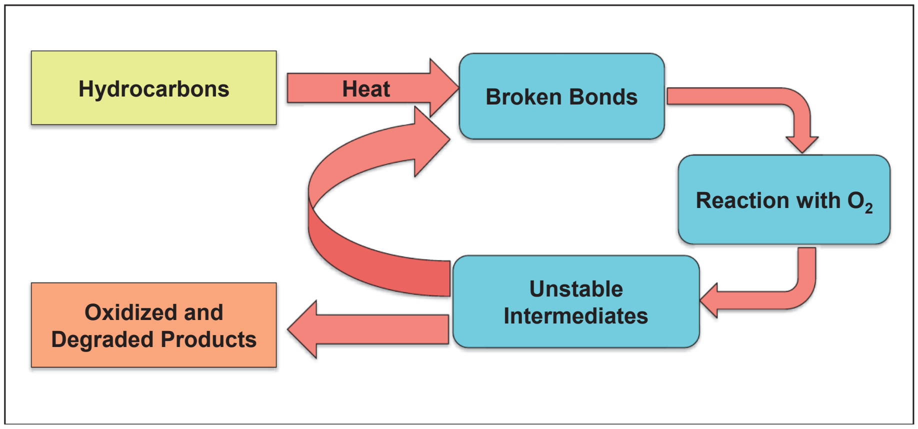

Figure 3 | **Thermal and oxidative stability. When the reaction follows the path of oxidation, it produces undesirable degraded products such as varnishes, lacquers and gums.** (*Courtesy of The Lubrizol Corp.*)

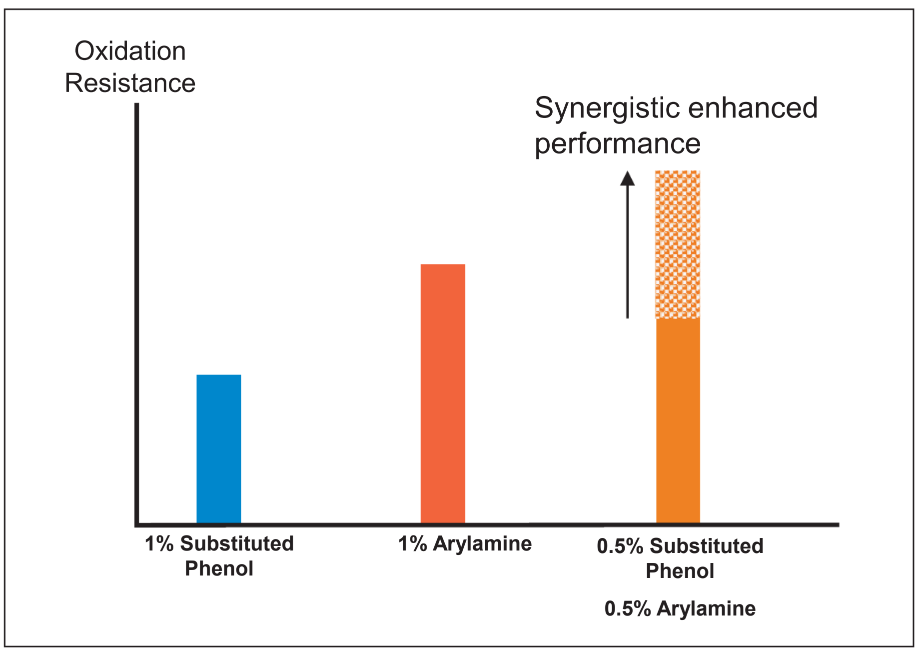

Figure 4 | **Oxidation inhibitor synergism. Oxidation resistance of the combined additives is substantially enhanced from the sum of the constituents.** (*Courtesy of The Lubrizol Corp.*)

protection" depends on film-forming additives that physically or chemically adsorb onto metal surfaces by their polar ends and associate with lubricant via their nonpolar ends to form a protective film.

Antiwear additives form a protective surface layer on metal, but it is not always a continuous film. Common phosphorus-containing antiwear agents include zinc dithiophosphates, amine thiophosphate and dialkyl hydrogen phosphite. Under higher temperatures and loads, these additives become activated and form discrete pad-like structures on surfaces instead of uniform layers, which help to separate them from mating metal parts. The surface reactive film of the pad-like structures is typically a polyphosphate iron oxide layer that forms a protective layer.

When multiple additives with varying reaction speeds and rates are together in a lubricating grease formulation, they compete with each other for access to locations on a metal surface. A lot of the additive in greases gets tangled up in the thickener, causing a controlled release-like event to take place. The additives are present but not all at the surface, and as the thickener is sheared down with use, more additives are released (*see Figure 5*).

The exact choice of additives for a lubricating grease will depend on the type and severity of the application as well as the nature of the base oil and thickener used. Synergistic or antagonistic reactions may arise between additives that will affect the quantities of these ingredients needed to meet a lubricant's performance goals. Typically the additive package for a multipurpose extreme pressure grease will contain five different additives comprising approximately 4% of the product weight.

Grease formulators can be thought of as chefs of the lubricant world, skillfully blending sometimes trifling quantities of ingredients to achieve memorable results. TLT

Multipurpose EP Grease: Typical Additive Package

	%wt
Extreme pressure	2.00
Antiwear agent	1.00
Rust inhibitor	0.60
Oxidation inhibitor	0.25
Metal deactivator	0.15
Total	**4.00**

Figure 5 | **Performance additives for greases.** (*Courtesy of The Lubrizol Corp.)*

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