Building a Better Base Fluid

Nearly all lubricating greases consist of three basic parts: a soap thickener, base stocks and chemical additives. According to the National Lubricating Grease Institute's annual Grease Production survey, more than 75 percent of the world's grease is thickened with lithium or lithium complex soaps, and over 90 percent is made with mineral base oils.

Lithium and lithium complex greases were patented in the 1940s — nearly 70 years ago — so the opportunities to improve them by tweaking the thickener systems have grown pretty slim, says Govind Khemchandani of Dow Chemical. However, there's still potential to boost lithium grease performance through the selection of additives and base stocks, he told the 2013 NLGI annual meeting in Tucson, Ariz. Of course, formulators have long turned to synthetic base stocks such as polyalphaolefins, polyalkylene glycols, organic esters and alkylated naphthalenes to boost performance beyond that of mineral oils.

For several years, the Freeport, Texas-based senior technical specialist and Ph.D. chemist has been working to persuade lubricant and grease manufacturers to expand this menu of base stock options to include oil soluble polyalkylene glycols. Less than a decade old, these newcomers (unlike older PAGs) can be blended with the paraffinic and naphthenic base oils which still account for over 90 percent of the world's lubricant applications.

Until this time, users who wanted to convert a piece of equipment from mineral oil to PAG lubrication had to repeatedly flush out the old material — an expense which somewhat dampened PAGs' appeal. "But the oil soluble version enables an easier conversion process for users who want to switch from a mineral oil fluid," Khemchandani said. There also was

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no way to boost mineral oil performance by incorporating some PAG into the base stock mix, the way blenders do with esters and polyalphaolefins.

That's changing now, he remarked. Recent experience is proving that lithium complex greases made with oil soluble PAG can bring strong benefits for end users, such as higher drop points, better friction properties, reduced volatility and greater solvency power. The latter especially helps control the formation of harmful deposits, sludge and varnish, he related to the NLGI meeting on June 18.

Oil soluble PAGs also offer gains for grease manufacturers themselves, Khemchandani later remarked to *Lubes'n'Greases*. The volume of soap needed to reach the desired consistency is lower with oil soluble PAG, and it's also easier to incorporate additive chemistries such as phenolic and aminic antioxidants into the grease because PAGs are highly polar in nature; that gives them better additive solvency. A lithium grease can be made more quickly and at a lower temperature as well, he said, because the higher solvency more rapidly dissolves hydroxy stearic acid — a key building block of lithium soap thickeners — and does it at a lower reaction temperature.

Using a lower reaction temperature has two direct benefits for grease manufacturers. It cuts their energy consumption and costs, and reduces the risk of "scorching" or oxidizing the soap thickener, Khemchandani pointed out. These are significant gains, since the thickener is often the most expensive component in the grease. The resulting soap fibers are more uniform in shape and size, too, giving the finished grease a smoother appearance.

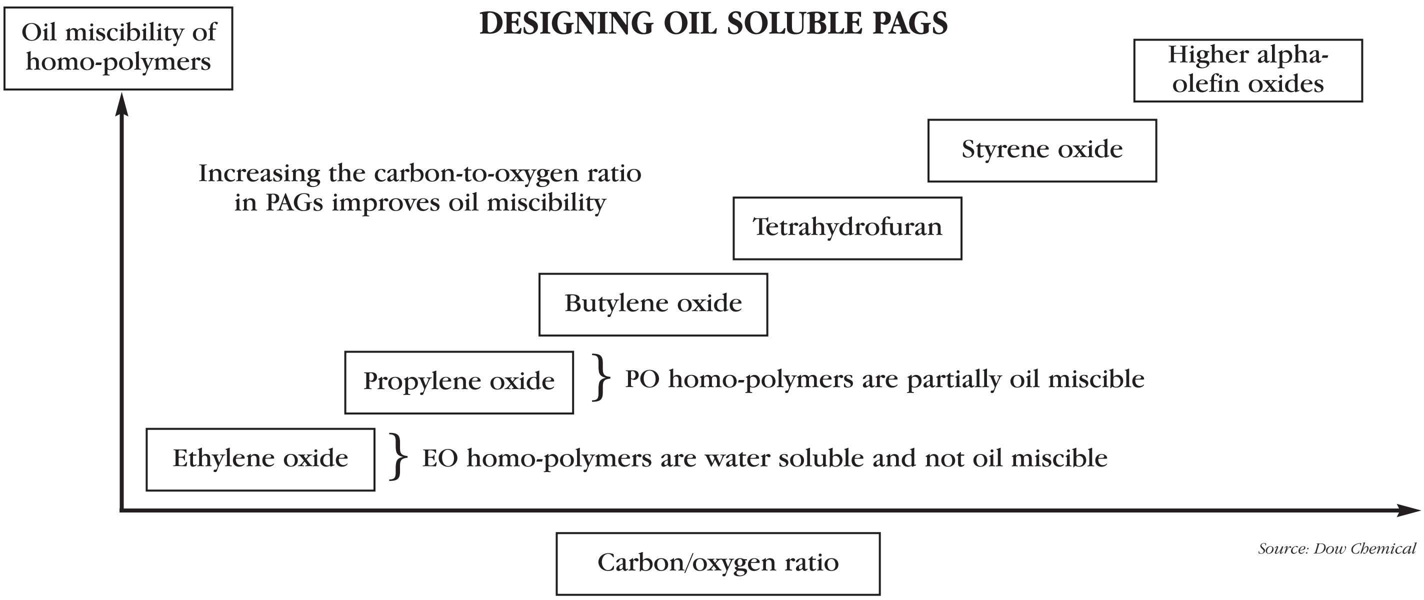
In fact, to reach NLGI 2 consistency, a grease made with oil soluble PAG needs to contain only about half the soap thickener of one made with PAO base fluid alone, Khemchandani showed the NLGI meeting, and one-third less soap than an NLGI 2 grease made with a blend of naphthenic and paraffinic base stocks.

Why do these PAGs differ from the older versions? Conventional PAGs are made through a high-pressure, catalytic reaction of epoxides — traditionally ethylene oxide and propylene oxide — with an initiator such as butanol, Khemchandani noted. This classic polymer structure is robust and flexible, and can be designed to have a wide range of molecular weights and viscosities, or to be water soluble or insoluble. PAGs can offer good film strength, temperature behavior and viscosity indices, and may also be designed to be biodegradable. All these variances are created by altering the ratio of the ethylene oxide to propylene oxide, the order in which they are combined or the catalyst employed.

Early PAGs were introduced into lubricant uses about 40 years ago, first as additives and viscosity builders in the 1960s. "In the 1970s, we began seeing the lubricity advantages of these fluids, although they were still mostly used as additives. Then, in the 1980s came the first use of PAGs as a primary base oils, in products such as gear and refrigeration oils," Khemchandani said. "From the 1990s and through today, PAGs have seen greater use as a base fluid. They're used now as hydraulic fluids, compressor oils, gas turbine oils and more."

They also found their way into lubricating greases, he added, but here they tended to be used as a high-end specialty, for example, to lubricate caliper brakes. "It still was not possible to use PAGs in general applications, for a number of reasons. The perceived negatives included hygroscopicity (which could lead to problems with corrosion), elastomer compatibility issues, and — the

DESIGNING OIL SOLUBLE PAGS



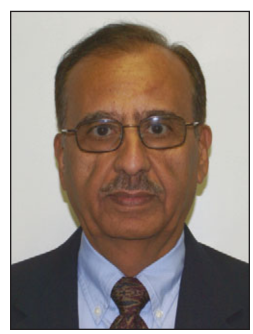
Source: Dow Chemical

biggest issue with PAGs — the impossibility of mixing with mineral oil based products." These perceptions tended to keep PAGs isolated in their own niche.

Seeking a PAG to overcome these drawbacks, Dow chemists found the key was to use higher alkoxides, such as butylene oxide and its derivatives, as the backbone for a new type of PAG molecule, rather than the simpler oxide mixtures. The world's largest manufacturer of PAGs, Dow is basic in butylene oxide, and since 2007 has commercialized a range of the oil soluble polymers with viscosities spanning from 18 cSt. to 680 cSt. at 40 degrees C.

Meanwhile, mineral oil technology also was changing, as refiners made highly pure, stable base oils such as API Group II and Group III, Khemchandani noted. "The refiners have done a great job of improving the oil's oxidative resistance, but at the same time, we've seen a decrease in solubility," he observed. Group II and III base stocks are highly nonpolar (a property they share with PAO), and while that makes them very stable it also has made it harder than ever to additize finished lubricants. Because oil soluble PAGs are polar and fully miscible with Group II, III and PAOs, they can be used either straight or as blend stocks to boost the overall solvency properties of finished lubricants.

In many ways, conventional and oil soluble PAGs are alike, but Khemchandani suggests that they should be regarded as separate chemistries to avoid confusion. Dow has trademarked its own oil soluble PAG base stocks as Ucon OSP, and makes them in North America and also in Europe. Ucon OSP is selling well in China, Europe and the United States, he told *Lubes'n'Greases*.



Govind Khemchandani

Greases are not the only product where oil soluble PAG is making a difference, Khemchandani went on. Other successes have come in paper-mill bearing lubricants, metalworking fluids, gas turbine oils and even high-performance racecars. In each case, the work began by understanding the exact problem that a lubricant formulator may face, and then selecting a PAG — conventional or oil soluble — to fit the need.

"In some cases, the blender won't use OSP as a 100 percent base oil, but perhaps as a component in their blends," he said. "Often, the first question in their mind is expense, but that's not a big drawback — it costs about the same as a high-vis PAO, in that price range."

Khemchandani also highlighted some of the similarities between oil soluble PAGs and PAOs. Both offer a low pour point and high viscosity index, he noted, "but one of the advantages of oil soluble PAG is that it also has excellent film-forming properties. And it will maintain these properties overall across a wide temperature range. So in an application that may currently use an ISO 46 viscosity grade, you might be able to use an ISO 32 grade with no loss of lubricating film." The lighter viscosity grade could help reduce the equipment's energy draw while still assuring durability, he said.

Another common formulating option has been to incorporate esters into lubricants to improve additive solubility, and that can be part of the solution too, Khemchandani agreed. "Yes, that gives some performance improvement, but you also can have risks regarding hydrolytic stability. But if you can add OSP you can improve this as well, because the OSP takes up the free water and holds it off the metal surface so it can't cause corrosion; the water stays attached to the main backbone of the molecule."

Someday, he concluded, it may be possible to go even higher up the molecular chain, to cyclohexene oxide or higher alpha olefin oxides, for further gains in PAG performance. Meanwhile, OSP has plenty of untapped potential to offer today's world of 90 percent mineral oil lubrication. ∎