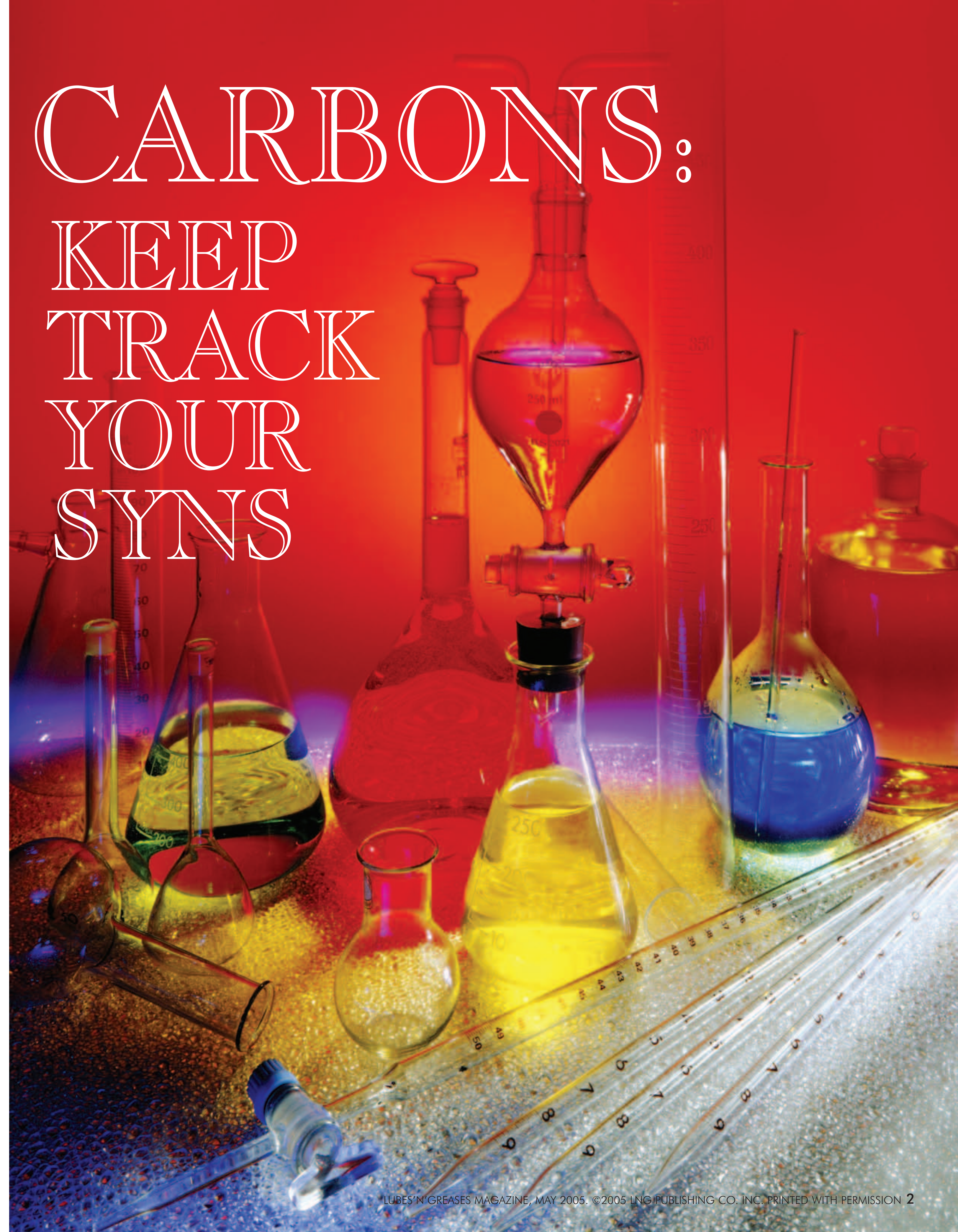
HYDROCARBONS: KEEP TRACK OF YOUR SYNS

Synthetic lubricants have always been intriguing for industry aficionados. For the general public, synthetics have an aura of high performance and racing quality, thanks to over 30 years of dedicated marketing effort. In most instances, the benefits are real, as requirements of highly demanding applications are often only met by use of synthetics.

By Ray Bergstra



Whenever the term "synthetic" is raised, some clarification is good. There are a number of guidelines that can be used to decide if a material should be referred to as synthetic but in general, synthetic materials are those that are manufactured by processes that involve chemical modifications to produce a fluid that is chemically altered from the feedstock.

Synthetic fluid types include esters, phosphate esters, glycols, polyethers, alkylated aromatics, silicones and others. This article will focus on the most versatile and highest volume group — the synthetic hydrocarbons, including the familiar chemistries of today (polyalphaolefins and Group III mineral oils) and the provocative ones of tomorrow (biorefined fluids, buckyballs and bicyclic compounds).

Since 1998, when the Better Business Bureaus' National Advertising Division ruled that lubricants made with API Group III base oils could be labeled as synthetic, the lubricants industry has kept a close watch on this market. There were adjustments, and some engine oil marketers in the premium price category sought to achieve higher margins by switching from polyalphaolefins (PAO) to less-expensive Group IIIs. However, the focus remains on delivering products of value to customers, and there has been an overall trend toward higher-quality base oils, led by new specifications for engine oils and transmission fluids. The result? The Group III market has grown, the PAO market has strengthened, and synthetic hydrocarbon based lubricants are finding new applications and continuous innovation.

GROUP III'S MUSCLE While products based on Group III technology are relatively new to the North American market, BP and Shell first proposed the synthetic nature of Group III stocks in Europe back in the 1980s. Their highly refined, high viscosity index base oils were used to formulate premium motor oils for high-performance European passenger cars.

Group III base oils continue to meet expectations in high-quality lubricants. Even if you don't wish to call them synthetic, there is no denying their cost vs. performance benefits. Group III stocks can't quite match the ultra-low-temperature fluidity of PAOs, but their high V.I. and purity still enable products to be formulated with fluidity down to -40 degrees C, the benchmark for cold-climate applications.

A look at lubricants from companies strongly invested in hydroisomerization and severe hydrotreating technology, such as Petro-Canada and ChevronTexaco, finds a range of premium products based on Group III base oils that provide excellent low-temperature viscometrics as well as oxidation stability. Group IIIs also have proven themselves in some of the most demanding applications, including Eaton's and Dana's long-drain specifications for on-highway truck transmissions, where ChevronTexaco's Delo Gear ESI is the only non-PAO based heavy-duty gear oil to win approval.

Further advances in Group III technology are expected to involve optimization of the various processes used throughout the industry, to either improve efficiency or enable the conversion of other paraffinic feedstocks to high V.I. base oils. In many cases, it's a matter of meeting market demand with existing assets or refining activity. For example, ExxonMobil's retrofitted Fawley, U.K., refinery recently came back onstream with a slack wax isomerization process. The base oils it now produces reportedly have V.I. in the 140 range, and Noack volatility between that of PAO and most Group III stocks.

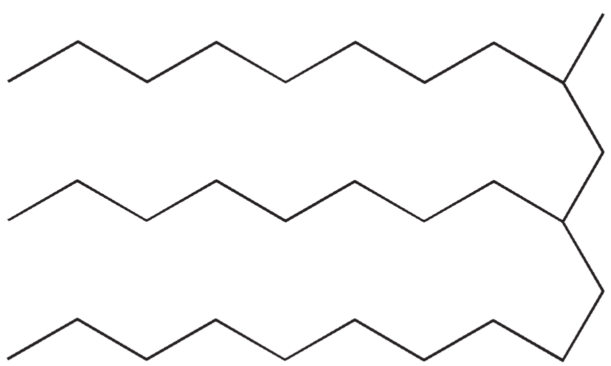
PAO HANGS TOUGH As Group III base oils made clear advances in the synthetic segment, particularly in North America, PAO manufacturers did not stand idly by.

PAOs have always been prominent in the world of synthetic hydrocarbon lubricants. Originally developed just prior to World War II, PAOs initially were recognized for their excellent low-temperature viscometrics, and were used in military applications such as tanks and aircraft where low-temperature fluidity was crucial. And it has been just over 30 years since Amsoil and Mobil first supplied automotive engine oils based on PAO to general consumers, who were eager to improve fuel economy during the 1970s energy crises. Since then, both the formulation technology and marketing strategy have matured. Today, lubricant manufacturers use PAO to develop and market a range of synthetic industrial oils, such as compressor oils, gear oils, hydraulic fluids and greases.

1-DECENE, C_{10} ALPHAOLEFIN

Figure 1

Linear alphaolefins such as decene molecules (above) can be built up into longer chains to make various grades of polyalphaolefins like the one below.



C_{30} PAO

PAOs typically are built up from the 10-carbon linear alphaolefin called decene (C_{10}), using a controlled polymerization process that produces the mixture of C_{30}, C_{40} and C_{50} molecules better known as 6 centiStoke PAO (see figure 1). This grade works very well for the manufacture of SAE 5W-30 motor oils. Through control of the manufacturing process, the C_{30}:C_{40}:C_{50} ratios in the final product can be adjusted to produce a 4 cSt PAO. This grade is useful for making SAE 0W-xx multigrade oils that still provide good volatility, shear stability and film thickness characteristics.

On the other hand, a manufacturer can also produce molecules with higher multiples of C_{10}, which provide heavier PAOs for higher viscosity weight lubricants. Further, the feedstock is not limited to decene; octene (C_8) or dodecene (C_{12}) linear alphaolefins can be used too.

"One of the main strengths of PAOs is the flexibility that they offer to product formulators," comments Chuck Bullock, PAO marketing manager for ExxonMobil Chemical. Its SpectraSyn line of PAO base oils, which range from 2 cSt to 100 cSt, was recently expanded to include beefier PAOs with viscosities of 150, 300 or even 1,000 cSt. Called SpectraSyn Ultra, these exhibit a number of interesting features including enduring film thickness at low sliding speeds.

Other PAO marketers also have announced additions to their product lines. Chevron Phillips Chemical Co. upgraded its Cedar Bayou, Texas, plant in 2000 to boost the oxidation stability of its Synfluid PAOs, and has developed fluids made from C_{12} alphaolefin. Although it is trying to sell or spin off its entire olefins business, BP has not shirked research either, and recently said it was adding a 140 cSt grade to its Durasyn line. ExxonMobil also is rolling out a new SpectraSyn Plus line of PAO, with improved viscosity and shear stability characteristics.

So although the premium lubricant market had to make room for products based on Group III base oil, Bullock says, "The PAO business has remained strong, with growth opportunities in each global region."

GTL WATCH With PAO and Group III products clearly established and growing, what new synthetic hydrocarbons are coming on stream? The main one to watch will be based on gas-to-liquids (GTL) technology. GTL technology is not so much about base oil performance — which is expected to rival that of Group IIIs — but rather the utilization of a process that does not involve crude oil.

GTL technology has been around for over 80 years, since its invention by German scientists Fischer and Tropsch. The process has three steps. The first is partial oxidation of hydrocarbon (natural gas) to hydrogen and carbon monoxide. This gas mixture is known as synthesis gas or syngas. The second stage involves catalytic polymerization of the syngas into heavier, largely paraffinic liquid (waxy) hydrocarbons. This is the Fischer-Tropsch reaction, the gas-to-liquids part. Stage three requires hydroisomerization of the waxy material to form cuts suitable for fuel and for lube base stocks. These base stocks are expected to be very pure, free of sulfur and with excellent volatility and viscosity characteristics — the very properties that synthetic lubricants boast.

Gregg Skledar, general manager of base oils for Sasol Chevron looks forward to the new fluids coming on stream. "GTL technology produces high quality base oils which offer lubricant formulators expanded opportunities to meet the ever increasing performance requirements for finished lubricants," he says.

To date only Shell has operated a GTL base oil plant, in Bintulu, Malaysia, and has done so since 1993. This small facility provided waxy raffinate feed for Shell's VHVI brand base oils. But this exclusivity will soon end as large investments in GTL plants are in play by the major integrated energy companies, to exploit previously unprofitable reserves of natural gas.

Shell, ExxonMobil and Sasol Chevron are all working separately with Qatar Petroleum for the construction of GTL plants in Qatar. ChevronTexaco has further investments with Sasol for a plant in Nigeria. These multibillion dollar affairs will clearly establish GTL base oils in the lubricant industry, around the end of this decade.

BIO, BUCKY AND BI-CYCLICS
An important aspect of GTL technology relates to the fact that any hydrocarbon source can be gasified to form the Fischer-Tropsch feedstocks of hydrogen and carbon monoxide. The U.S. National Renewable Energy Laboratory and other research organizations have developed a "biorefinery" model that does this exact thing. Here, the crude hydrocarbon feedstock is biomass, essentially any type of plant fiber. The abundance of biomass waste from agriculture and forestry processing plants (i.e., wood byproducts, corn cobs, grain hulls) can provide viable feed for gasification to "biosyngas" and subsequent GTL synthesis.

The location and proliferation of these types of plants will depend on global economic conditions, particularly with respect to the decline of fossil fuel availability, but the biorefining concept is considered viable and is exciting from an environmental standpoint.

In addition to innovations relating to the more conventional paraffin and isoparaffinic synthetic hydrocarbons, there are completely novel structures. We have all heard of buckminsterfullerene, or "buckyballs," soccer ball-like structures that are known to have high levels of stability and could act like "liquid ball bearings," some say. However, things have been very quiet on this for a decade, with no sign of commercial-scale activity as a lubricant.

Meanwhile, new fluids have recently been developed for continuously variable transmission (CVT) technology. These are traction fluids, and both Idemitsu and General Motors have patent coverage for a range of synthesized bi-cyclic hydrocarbons as part of their respective CVT development programs. Idemitsu has commercialized its product under the Apollo brand. These fluids are not buckyballs but have a rigid three-dimensional structure (figure 2) and are comprised of dimerized bicycloheptanes.

While this novel synthetic hydrocarbon may be expected to be costly, the basic feedstocks (dicyclopentadiene and isobutylene) are available in industrial quantities at approximately 30 cents per pound. With a little heat and pressure, these two molecules can be convinced to join together to form the desired bicycloheptene, in what is known as the Diels-Alder reaction (the second pair of German chemists honored in this article). The bicycloheptene is then dimerized to form the desired bridged bicycloheptane.

"These new classes of patented traction fluids offer potential advantages in toroidal-CVT performance due to their improved low-temperature fluidity, thermal stability and high traction coefficients," explains Tom Chapaton at GM Research. "With their unique properties, these fluids may also find other industrial applications."

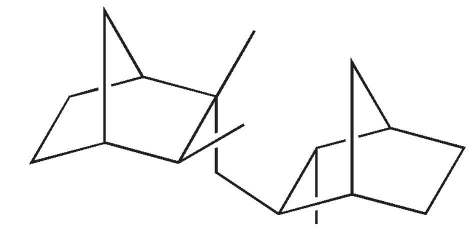


Figure 2

Synthetic cyclic hydrocarbons, with their three-dimensional shape, can be designed to perform as traction fluids.

Another traction fluid based on a synthetic cyclic hydrocarbon is made by Findett Corp.'s Santotrac division, and is being used in the heavy-duty CVT from Orbital Traction Ltd. in the U.K., as well as some motorcycles.

Biorefining, GTL, high V.I. PAO, bi-cyclic traction fluids: new structures, new feedstocks, new processes. Synthetic fluids continue to be exciting technologies with innovation as the key. And this is all made possible how? It's because every carbon atom makes four bonds. When you have 50 of them in one molecule, that makes for lots of possibilities and opportunities. And when it comes to lubricants, to syn is a good thing. ∎

COUNT YOUR SYNS

How many can you come up with? Here's a mere smattering of brands that trumpet their syn-ful nature:

SpectraSyn	Synoil
Supersyn	Synlube
Durasyn	Synesstic
Syntheso	Firesyn
Isosyn	Puresyn
Syntec	Syntroil
Powersyn	Synfluid
Syncomp	Aqua Syn
Ultrasyn	Synduro
Synquest	Synalox
Hydrasyn	Synergel
Synpower	Synergol
Coolsyn	Synturo

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