SYNTHETIC LUBRICANTS AND THEIR LONG-TERM EFFICIENCY AND SUSTAINABILITY

Plagued with numerous instances of political, technical, and environmental difficulty, the lubricating oil industry has proven to be impressively resilient. But why wouldn't they be? Lubricating engine oils are a component of virtually every vehicle on the road around the globe, and in nations where a large share of the population owns at least one vehicle or uses public transit such as a city bus, it's no surprise that these products are something virtually every consumer uses, whether they realize it or not. Over the course of around 120 years, the lubricating engine oil market has shifted from simple (or straight) mineral oils to complex proprietary blends of artificially synthesized and polymerized molecules, known as synthetic oil. At a glance, mineral and synthetic oils appear to be virtually identical in both form and function, but while the former will deteriorate as it is used, the latter is specially formulated to ensure that the oil will last significantly longer, lubricity is better retained, and result in better fuel economy. But what are "synthetic" oils and how did they become the oil of choice for numerous auto manufacturers today?

With the rise of increasingly complicated engine design and ambitious emissions standards, synthetic oils have risen to the forefront for use in automobiles around the world, but these oils are nothing new. Before World War II, the Germans worked to develop synthetic oil when their crude oil supply was severely limited by the Allied forces. Simultaneously, the United States began research and development into synthetic base oils, with Standard Oil of Indiana (now Amoco) marketing a version of synthetic oil (composed of polymerized olefins) as early as 1929 [1]. Other developments from this time period include polyalkylene glycols (PAGs) by Union carbide and I.G. Farben and synthetic esters by I.G. Farben. Development of synthetic lubricants and fuels such as these was of high significance in the 1930s and 1940s due to the foreseeable scarcity in a potential future war, at least for Germany. German researcher Dr. Hermann Zorn [2] began development of synthetic lubricants in an attempt to retain the ideal properties of natural mineral oil while reducing the drawbacks. By the 1940's, he had developed over 3,500 different blends of polyolesters and diesters with poly(ethylenes) from Fischer-Tropsch synthesis. The esters were in Germany also used to up-grade mineral oils, when available due to scarcity. They were standardized for all military services as SSxxxx grades (SS in this case stands for Synthetischer Schmierstoff, or "synthetic lubricant"). Synthetic lubricants were first used during World War II by both Germany (blends with esters) and the US as PAG-based aircraft engine oils from March 1944 onward [3]. Dr. William Albert Zisman of U.S. Naval Research Laboratory was the counterpart in ester development, but synthetic esters began to be used in jet turbines in the 1950s and 1960s due to their superior oxidation stability and continue to be used today [4].

When the Organization of Arab Petroleum Exporting Countries (OAPEC) placed an oil embargo on several countries, including the US and UK, oil prices skyrocketed and consumers embarked on a search for smaller, more fuel-efficient vehicles. That same year, Mobil unveiled Mobil 1 synthetic engine oil in Europe, composed of PAO and an ester (trimethylolpropane (TMP$_{-C8-10}$), which was marketed as a fuel-saving alternative to conventional mineral oil [6]. This became an instant success across Western Europe and was unveiled globally in 1974 [5]. The oil crisis unintentionally acted as the launch for commercial and consumer use of synthetic oil, and the superior performance of these oils only helped them further permeate through the market. In 1989, Mobil collaborated with BMW to conduct the "Million Miles Test", a test in which Mobil 1 synthetic oil was used as the motor oil in a new BMW 325i and then run for 1 million miles (around 4 years straight), making sure to follow the manufacturer's recommended service schedule, resulting in an oil change every 7,500 miles, which consumed approximately 600 litres of engine oil. Upon disassembly, no significant signs of damage or wear were observed. This enabled Mobil 1® to become the recommended oil for every Porsche produced during or after 1996, several Mercedes models, and a multitude of other vehicles.

Figure 1: API classification of base groups

Classification	Description	Saturates [%] (ASTM D2007)	Sulfur [%] (ASTM D1552, etc.)	Viscosity index VI (ASTM D2270)
Group I	(Conventional, solvent refined)*	<90	>0.03	80-120
Group II	(Hydro-processed)*	≥90	≤0.03	80-120
Group II+	(Hydro-processed)*			>100-115
Group III	(Severely hydro-processed or isomerized wax)*	≥90	≤0.03	≥120
Group III+				>130-140
Group IV	Polyalphaolefins	_	_	≥120*
Group V	All other base stocks not included in Groups I to IV	_	_	_
Group VI#	Polyinternalolefins	_	_	_

*- comments in parenthesis or values are not included in the original API definitions

\# Europe only (ATIEL: Association technique de l'industrie européenne des lubrifiants)

♣ Group II+ and III+ are unofficial groups and used for marketing purposes.

In response to the widespread popularity of synthetic and synthetic blend oils, the American Petroleum Institute (API) created a series of 5 oil groups in 1993 [7]. These groups are based on key properties of the oil and are shown in Figure 1. These groups take sulphur and saturates content and viscosity index into account as well. Group I and Group II are made up of base oils that are derived from crude oils, where Group 1 is solvent refined and Group II is hydrotreated. Group III oils are also derived from crude oils but may be marketed as "synthetic blend" oils due to their high level of refinement [8]. These oils are typically hydrocracked. Group IV and Group V are comprised of synthetic base-oils, where Group IV oils are only made of polyalphaolefin (PAO) oils. Other synthetic base-oils are placed in Group V, which in other words can be best described as "synthetic but not made up of PAO oils". Evolutions in process technology and market demands led to the proliferation of Group II+ and Group III+, which differentiate themselves from their parent group by higher viscosity indices. These groups are not formally listed in the API literature, but are used for marketing purposes.

To elaborate on synthetics, a Group IV oil is made up of PAOs, but what is a "PAO"? Polyalphaolefins are manufactured hydrocarbons that are created by catalytic oligomerization polymerization to create low molecular weight linear olefins, most commonly C_{10} or C_{12} carbon. This sounds very specific, and you may be wondering, *why is Group V so vague by comparison?* The Technical Association of the European Lubricants Industry (ATIEL) sought to resolve some of this vagueness by introducing their own Group VI category, which was comprised of polyinternalolefin (PIO) oils. These oils are synthesized from linear olefins of C_{15} and C_{16} carbon. Group VI (shown in Figure 1) became obsolete in 2010, as PIOs seized production.

Polyalphaolefins and polyinternalolefins may be in different API (and ATIEL) Groups, but both are considered to be non-polar synthetic. Another type of synthetic oil is a polar synthetic base stock. These stocks consist of carbon, hydrogen, and oxygen and are polarized by a series of ester or carboxylic linkages. Esters are a common component in synthetic oils, with the most common esters including Di-isotridecyladipate (DITA), Trimethylolpropane ester (TMP-(C_8-C_{10})$_3$), and Pentaerythritol tetraester (PE-(C_5-C_{10})$_4$). Another type of polymer used in polar base stocks is polyalkylene glycol. Polyalkylene glycols (PAGs) are a group of synthetic polymers built from a combination of ethylene oxide (EO) and propylene oxide (PO) monomers polymerized from a starter molecule, often n-butanol.

With so many varieties of base stocks available, standardization and categorization became a necessity [9]. Following the API's introduction of base oil groups in 1993, the European Automobile Manufacturers' Association (ACEA) introduced its first set of oil sequences in 1996. These sequences set date ranges that oil must be marketed and sold during in order to claim ACEA compliance [10]. This is done similarly to the International Lubricant Specification Advisory Committee (ILSAC) ratings in that the current standards are reassessed after a couple years, updated to a new standard, and then declared obsolete.

These standardizations may appear to be beneficial in that they force oil producers to be proactive in producing oil products that exceed expectations in anticipation of the next ACEA or ILSAC standard. Despite this speculation making sense in theory, reality paints a different picture, an idea shown by the split in the ILSAC GF-6 specification. Many Japanese automakers have started producing international-market cars that utilize the thinner-than-ever 0W-16 oil, but domestically, the development of 0W-16 engine oils and grades as thin as 0W-12 and 0W-8 was anticipated and marketed by Japanese automakers. 0W-16 has existed in Japan for around 20 years, but is something new to markets elsewhere, so new in fact that the International Lubricants Standardization and Approval Committee (ILSAC) created a separate standard for 0W-16 oil. The ILSAC GF-6 specification is split into GF-6A (HTHS >2.6 mPas) and GF-6B (HTHS 2.3-2.6 mPas) to accommodate for 0W-16. The split is caused from the fact that SAE 16 grade is such a new oil viscosity rating. The same split occurred for truck Diesel engine oils in API CK-4 (HTHS >3.5 mPas) and API FA-4 (HTHS 2.9-3.2 mPas). This also marks both GF-6A and CK-4 as the first API standards to not be completely backwards compatible (GF-6A is backwards compatible for all included oil grades except 0W-16), due to their reduced HTHS. For reference, the SAE 0W-20 grade was formerly the thinnest grade recognized by the Society of Automotive Engineers (SAE), and this rating was added to the list of SAE Viscosity grades over 30 years ago [12]. This sounds like a good thing: oil standards became outdated, and ILSAC updated them. But when further explored, this is a lot more complicated. Japanese automakers may be setting the trend with new thinner oils such as 0W-16, but these are not the only new oils being introduced before a specification outside of Japan is ready for them. The Japanese Automobile Manufacturers Association (JAMA) recently proposed a 0W-8 viscosity rating for use in automobiles of which an HTHS at 150°C of 1.7-2.0 mPas is close to the that of water at 20°C. The difficulty here is in approving these rating before its entry into the international market. When 0W-20 oil began entering markets, it had already been a part of the list of recognized SAE oil viscosities for just shy of two decades [9]. This is in stark contrast to 0W-16, which began selling on models such as the Toyota Camry and Honda Fit in the United States as early as July 2017 and in Western Europe since April 2019, despite the ILSAC GF-6 specifications not taking effect until May 2020. Satoshi Hirano of Toyota Motor Corporation claims that "0W-8 technology is almost ready" for consumer use, but will likely not be certified by ILSAC until the future ILSAC GF-7 or ILSAC GF-8 (if not later), which is not expected to occur until 2023 at the earliest, and likely much later based on the typical time interval between ILSAC standards.

Table 1. Base Oil Standards for ACEA and ILSAC [10,11]

ACEA Engine Oil Sequences

Issue Year	Introduction	Obsolete
1996	Mar 1996	Mar 2000
1998	Mar 1998	Mar 2002
1999	Sep 1999	Feb 2004
2002	Feb 2002	Nov 2006
2004	Nov 2004	Dec 2009
2007	Feb 2007	Dec 2010
2008	Dec 2008	Dec 2012
2010	Dec 2010	Dec 2014
2012	Dec 2012	Dec 2016
2016	Dec 2016	*Rev. 3*

ILSAC Standards

Standard	Introduction	Obsolete
ILSAC GF-1	Oct 1990 (Rev. Oct 1992)	Aug 1997
ILSAC GF-2	Nov 1995	Mar 2002
ILSAC GF-3	Jul 2001	Apr 2004
ILSAC GF-4	Nov 2004	Sep 2011
ILSAC GF-5	Oct 2010	May 2021
ILSAC GF-6A, ILSAC GF-6B	May 2020	*Still In effect*

The miscibility of esters with hydrocarbons is a clear benefit of esters over traditional polyglycols (PAGs). Following Mobil 1, hydrocarbon ester blends with higher ester contents meeting the bio-no-tox or eco-toxicological criteria were proposed by end of the 1990s (Castrol Greentec LS, ELF Victory HTX 822 or BP Vistra 7000 und FUCHS Titan GT1), but the prices of these environmentally friendly offers were prohibitive for the market penetration. Nowadays PAGs based on butylene oxide and mixtures of butylene oxide/propylene oxide as well as those started from long chain alcohols are oil soluble and enables the application of PAGs as co-base stocks in hydrocarbons. Within base stocks, PAGs offer the highest intrinsic viscosity indices and lowest coefficients of friction.

The reduction of CO_2 emissions from motor vehicles is the strongest motivation, but one hinderance in the delay of development of thinner motor oils may be fears on durability, especially in highly downsized engines, which require new materials and/or tighter tolerances in machining. Hybrid technology has become a rapidly growing technology for use in auto engines over the past 20 years, with the earliest versions originating from Japan in the early 2000s (Honda Insight and Toyota Prius). Today, virtually every automaker offers hybrid drivetrains in their vehicle lineup that combine downsized combustion engines with electric motors. These technological advancements are great for reducing emissions and increasing fuel economy, but manufacturers also rely on components beyond the engine itself, notably the oil they recommend for use in those engines. Thinner engine oils reduce the friction between components within an engine, resulting in a lower amount of energy loss, increasing the efficiency of the engine [13]. These developments have shifted largely in favor of 0W-20 over the past two decades and, as previously mentioned, have even begun shifting to thinner oils such as 0W-16. It's only a matter of time before automakers begin recommending viscosities such as 0W-8, but the development of engines optimized for 0W-8 may be slowed by the lack of a standard or specification for such an oil. This delay in implementation and pause in the development of these thinner oils may have major impacts on fuel emission standards and the overall sustainability of automobiles going into the 2020s and 2030s. Physical evaporation anticipates alternative base oils, since the NOACK evaporation of low viscosity hydrocarbons increases with decreasing molar mass of the base oil backbone. The molecular polarities originated from oxygen in the backbone of esters and PAGs increase the intermolecular attraction and thus reduce volatility and increase viscosity index.

Despite some delays in the development of thinner oils, a new class of lubricants called "sustainable lubricants" is currently on the horizon (independent of oil group or viscosity). These will have different requirements than the already-implemented Environmentally Acceptable Lubricants (EALs) or biolubricants as per EN16807. EALs primarily focus on human and environmental toxicology (in effect, "what happens after the oil is discarded?") in addition to ultimate/ready biodegradation, whereas sustainable lubricants are aimed at increasing the use of renewable resources, reducing waste by longer drains and increasing recycling by re-refining. On the other hand, friction reduction is a clear benefit in any life cycle analysis and is covered by United Nations sustainable development goals (SDG) #7 and #13. Friction reduction for sustainable lubricants is still an unaltered property or "must have". Sustainable lubricants will also focus on the carbon dioxide emissions during their whole lifecycle and the consumption of resources with respect to their lifetime and the generation of individual carbon dioxide emissions as a result (recycling and re-use of used oils as resources as per SDG #12).

The continued use of EALs and the introduction of sustainable lubricants are excellent steps towards making the lubrication industry more sustainable and more efficient. The need for low and ultra-viscosity lubricants with preferably a high intrinsic viscosity index associated with low NOACK evaporations favor synthetic base stocks over conventional mineral oil. Development and legislation with regards to material sustainability will likely continue over the course of the coming years promoted by the awareness of end users, but other standard issues, such as ILSAC's GF-6A and 6B standards lagging behind the market, may also slow the widespread development and implementation of stricter emissions standards. Only time will tell, if ILSAC GF-7 will include thinner oil viscosities and whether or not those oils will enter widespread use in the market, but one thing is certain: the sustainability and energy efficiency of lubricating oils through lower fiction is a key component that will shape where the industry moves.

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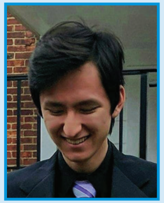
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