CHAPTER 11
LUBRICATING OIL BLENDING

Lubricating oils are designed to perform several jobs in engines and other industrial machines. These are lubrication of moving parts, cooling, cleaning and corrosion control. Lube base stocks produced by refineries and petrochemical manufacturers (synthetic lube base stocks) are used to produce a large number of products such as the following:

- Gasoline and diesel engine oils
- Agricultural engine oils
- Marine engine oils
- Aviation and turbine oils
- Hydraulic and transmission oils
- Gear oils
- Automotive and industrial greases
- Metal working oils
- Electrical insulating oils
- White mineral oils
- Process oils

Automotive engine oils, transmission oils, and gear lubricants constitute roughly two-thirds of the total lube oils produced. Most of these products are prepared by blending an appropriate percentage of additives with lube base stocks. For every application, the base stock and additive package has to be carefully selected to meet the compatibility and requirements of the intended application.

CLASSIFICATION OF LUBRICATING OILS

Lubricating oils and greases can be classified in many ways; by their end use, by viscosity grades, by their additives package, or by their producers' brand names. The most popular classification of lubes is according to their usage:

- Engine oils (petrol and diesel engines, aircraft, marine engines)
- Turbine oils
- Gear oils
- Compressor (refrigeration, air) oils
- Quench oils used in metalworking
- Cutting oils (in metal cutting)
- Insulating oils used in transformer and circuit breakers
- Wire rope lubricants
- Chain lubricants
- Hydraulic oils

The type of base oil (naphthenic, paraffinic, or synthetic) and additives may vary to provide the qualities required for a given application.

CLASSIFICATION BY VISCOSITY

Classification according to viscosity has been done by these professional societies and organizations:

- SAE (Society of Automotive Engineers, USA)
- API (American Petroleum Institute)
- AGMA (American Gear Manufacturers Association)
- NLGI (National Lubricating Grease Institute)

INTERNATIONAL STANDARDS

For industrial lubricants, many different classification systems have been used in the past in different parts of the world. In 1972, a worldwide viscosity classification system for industrial lubricants came into place. Table 11-1 shows the current International Standards Organizations (ISO) 3448 viscosity classification system. The classification is based on series of viscosity grades, each being approximately 50 percent more viscous than the preceding grade. Viscosity variation within the grade is plus or minus 10 percent of the nominal viscosity of the grade. For lubricating oils other than automotive oils, the ISO VG classification system is generally used. This classification is in terms of viscosity only; other characteristics are not considered. Each ISO viscosity grade number corresponds to the midpoint of the viscosity range expressed in centistokes (cSt) at 40°C. For example, a lubricant with an ISO grade viscosity of 100 has a viscosity in the range of 90 to 110, with 100 the midpoint of the range.

CLASSIFICATION BY ADDITIVE TYPES

Lube oils may be classified by additive type as follows:

- Inhibited or RO (rust and oxidation inhibitor containing additives)
- Anti-wear (AW) containing lube oils
- Lubes with extreme pressure (EP) additives
- Compounded oils: containing 3 to 10 percent fatty or synthetic fatty oils
- Residual compounds: These are heavy-grade straight mineral oils with asphaltic component for open gear application where tackiness is required to increase adhesion

AUTOMOTIVE ENGINE OILS

Viscosity is considered the most important single property of lubricating oils. Automotive crankcase and gear oils used in gasoline and diesel engine lubrication have been classified by the SAE (Society of Automotive Engineers, USA) in terms of viscosity. The viscosity classification takes into account the temperature at which the oils are to be used. In 1911, the SAE developed the SAE J300 standard that specifies engine oil viscosity classification. The SAE viscosity rating was based on average time, in seconds, for a specific quantity of motor oil at 212°F to flow through a test apparatus or viscometer with an orifice of a specified diameter. An SAE viscosity number, according to SAE J300, was the average time and not an exact measure. For example, any oil that took 5 to 15 s to flow would be

TABLE 11-1 Nonautomotive Lubricating Oils ISO Viscosity Grades

ISO grade	Midpoint viscosity at 40°C cSt	Viscosity at 40°C		Viscosity at 37.8°C		Approximate viscosity at 98.9°C, SUS		Approximate viscosity at 98.9°C, SUS		Approximate viscosity at 98.9°C, SUS	
		Min. cSt	Max. cSt	Min. SUS	Max. SUS	95 VI Min.	Max.	65 VI Min.	Max.	35 VI Min.	Max.
2	2.2	1.98	2.42	32.8	34.4						
3	3.2	2.88	3.52	36	38.2						
5	4.6	4.14	5.06	40.4	43.5						
7	6.8	6.12	7.48	47.2	52						
10	10	9	11	57.6	65.4	34.6	35.7	34.2	35.3	33.8	34.9
15	15	13.5	16.5	75.8	89.1	37	38.3	36.4	37.8	36	37.3
22	22	19.8	24.2	105	126	39.7	41.4	39.1	40.6	38.5	40
32	32	28.8	35.2	149	182	42.9	45	42	43.8	41.4	42.9
46	46	41.4	50.6	214	262	47.1	49.9	45.4	47.8	44.2	46.2
68	68	61.2	74.8	317	389	53	56.9	50.3	53.4	48.6	51.1
100	100	90	110	469	575	61.4	66.9	56.8	61	54	57.2
150	150	135	165	708	869	74	81.9	66.6	72.7	62.1	67.2
220	220	198	242	1046	1283	90.3	101	79.3	87.6	72.6	79.5
320	320	288	352	1531	1878	112	126	95.7	106	86.3	95.3
460	460	414	506	2216	2717	139	158	116	130	104	115
680	680	612	748	3298	4046	178	202	145	162	127	142
1000	1000	900	1100	4885	5994	227	257	181	204	156	175
1500	1500	1350	1650	7385	9063	293	331	229	256	204	219

ISO classification of viscosity is issued by International Organization for Standardization, as ISO 3448, BS 2431.
The system classifies industrial lubricating oils into ranges by their nominal kinematic viscosity at 40°C (104°F).
Each range is identified by an ISO VG, viscosity grade, number that corresponds to midpoint viscosity of its range in centistokes.

TABLE 11-2 SAE J 300 Engine Oil Viscosity Specifications*

SAE viscosity grade	Cold cranking max. viscosity		Cold pumping max. viscosity		Viscosity, cSt at 100°C		Hot/High shear viscosity at 150°C
	cP†	at, °C	cP	at, °C	Min.	Max.	cP
0 W	6200	–35	60,000	–40	3.8		
5 W	6600	–30	60,000	–35	3.8		
10 W	7000	–25	60,000	–30	4.1		
15 W	7000	–20	60,000	–25	5.6		
20 W	9500	–15	60,000	–20	5.6		
25 W	13000	–10	60,000	–15	9.3		
20					5.6	9.3	2.6
30					9.3	12.5	2.9
40					12.5	16.3	3.7
50					16.3	21.9	3.7
60					21.9	26.1	3.7

*Revised December 1999.
†CentiPoise.

rated as SAE 10. Similarly, oil that took 25 to 34 s would be SAE 30, and so on. At that time, only SAE 10, 20, 30, 40, and 50 grades existed. There were no SAE 0 or SAE 60 or winter grades as in the present classification. Over the years SAE J300 standards were amended many times with advances in automobile design. SAE grade 60 was added as the need for thicker oil in aviation and heavy-duty engines became apparent. SAE W grades were added as it became apparent that engines could not be started in cold winter conditions with some SAE 30 oils. Table 11-2 shows the SAE classification for crankcase oils.

Multigrade Engine Oils

A multigrade engine oil such as SAE 10W/30 has the viscosity characteristics of both SAE 10W and SAE 30 oil. Similarly, the multigrade grade oil SAE 80W/90 has the viscosity characteristics of SAE 80W and SAE 90 gear oils. Today, most automobiles and trucks use what is termed "multiviscosity oils." These are in fact multigrade, not multiviscosity, oils. An oil cannot be multiviscosity, but it can be multigrade. For example, an SAE 10W40 oil meets the viscosity requirements of SAE 40 oil and also that of subzero grade SAE 10W. This implies that oil will flow like SAE 10W oil at a low ambient temperature such as during cold starting. Referring to Table 11-2, an SAE 10W oil will have a viscosity not greater than 7000 cSt at –25°C (for cold cranking) and not more than 60,000 cSt at –30°C to facilitate the flow of oil to the engine during cold weather. Multigrade lubricating oils are manufactured by blending a low-viscosity base stock oil with a viscosity index improver additive. These are polymer additives that produce a thickening effect at high temperatures but are dormant at low temperatures. In multigrade oils, polymers are added to light base stock that prevent the oil from thinning out at a fast rate as the oil warms up. At low temperatures, the polymer molecules are coiled up and allow the oil to flow without freezing. As the oil warms up, the polymer molecules begin to unwind into a long chain that prevents the oil from thinning at a rapid rate with the temperature increase. Multigrade oils are one of the greatest advancements in lube formulation, but they should be chosen with caution. It is appropriate to choose a multigrade oil with the narrowest span of viscosity appropriate for the highest and lowest ambient temperature in summer and winter driving conditions. Lubricating oil with a minimum amount of polymers is better for the engine. In actual use in engines, polymers can shear and burn, forming deposits that can cause sticking and other problems in engines. For example, if we compare the two lube oils 10W-40 and 20W-50, both oils have a 30-point spread, but because 20W-50 starts with a heavier base oil, it requires less of a viscosity index improver (polymer) to meet the specifications and thus is preferable. The wide viscosity range oils with their higher polymer content are more prone to viscosity and thermal breakdown. It is the oil that lubricates, and additives do not play any part in it. The oils with the minimum of additives are the best. The optimum viscosity grade for a given application depends on the ambient conditions and the type of engine used.

Neat Engine Oils

In certain applications, multigrade engine oils with a high VI additive content is not desirable. These include high r/min, high-load engines such as lawn mowers, high horsepower racing cars, and diesel engines. Lubricants such as SAE 30 or SAE 40 are recommended because these engines operate under a very high r/min, load, and heat conditions and, in the case of small engines, they are air cooled. VI additives are a weak link in the lube. VI additives under extreme heat, load, and shear condition tend to depolymerize, resulting in failure to reach their intended high-temperature viscosity. As the shearing continues, loss of oil film, increased wear rates, high oil consumption, or engine failure may result. Use of synthetic (PAO, esters) base oil lubes with very high VI (120+) is increasing in this segment.

Optimum Viscosity Grade

The ideal viscosity for motor oil in piston engines operating at normal engine operating conditions is equivalent to SAE 30 (9 to –12 cSt at 100°C). If a thinner oil is used, say SAE 20, there will be less resistance to motion due to reduced viscosity and therefore better fuel economy. However, this gain in fuel economy does not occur without cost due to the following factors:

- Lower viscosity and higher volatility results in greater oil consumption.
- Decrease in engine service life due to increased engine wear under the same operating conditions. It is estimated that the gain in term of better mileage by using SAE-20 instead of SAE-30 may be less than 1 percent, whereas the reduction in engine life may be on the order of 30 percent.

If a heavier oil (SAE 40 or SAE 50) is used under normal operating conditions, there will be more resistance to motion due to increased viscosity, resulting in poorer fuel economy. The loss in fuel economy is somewhat compensated for by the following:

- Decrease in oil consumption due to higher viscosity
- Decrease in oil consumption due to lower volatility
- Increase in engine service life due to reduced engine wear

Most heavy-duty engine manufacturers recommend SAE-40, 15W-40, or 5W-40 oils. If the ambient or the operating temperature is increased from ideal or normal (70°F), oil viscosity must be increased to assure same level of protection from engine wear, thus SAE 40 for 100°F and SAE 50 oils for 120°F ambient temperatures. Heavier grades are also desirable for towing and heavy loads. If the engine speed is increased during long-distance high-speed driving in low ambient temperatures, lower viscosity oils such as SAE-20 could be used in place of SAE-30 (in manual transmission cars where vehicle speed is proportional to engine r/min). If the load is decreased, oil viscosity can be decreased without any penalty. Long-term durability of the engine is related to high temperature/high shear specifications in SAE J300 standards. For SAE-20 it is 2.6 cP minimum at 150°C. For SAE-30, it is 2.9 cP (minimum). For SAE-40 oil, there are two specifications: 2.9 cP, which is the same as that for SAE-30, and 3.7 cP, which is the same as those for SAE-50 and SAE-60. The first specification is for light-duty engines (service life, 100,000 to 150,000 miles), and the second specification is for heavy-duty engines (service life, up to 1,000,000 miles). These oils are labeled as "HD" oils. Heavy-duty oils must meet the second SAE-40 specification of 3.7 cP, minimum, at 150°C. (Refer to Table 11-3 for a list of the optimum motor oil grades.)

TABLE 11-3 Optimum Motor Oil Grades

SAE viscosity grade	Temperature conditions for use, °F	Recommendations for use
5W–30	<0	Provide excellent fuel economy and low-temperature performance.
10W–30	>0	Most frequently recommended viscosity grade for most automobile engines, including high-performance multivalve engines and turbocharged engines.
10W–40	<0	For greater protection against engine wear and oil breakdown from oxidation.
20W–50	>20	Maximum protection for high-performance, high r/min racing engines.
30	>40	For high temperatures and heavy loads, such as driving in the desert or towing a trailer at high speeds for long periods.

EFFECT OF VISCOSITY ON FUEL ECONOMY

For a vehicle to economize on fuel, frictional losses in engine must be cut to minimum. Fuel economy improves when more energy goes into propelling the vehicle and less energy is used in overcoming frictional losses in the engine. This may include oil film resistance between moving parts, and the friction reduction must be maintained through changes in speed, shear stress, and temperature. In passenger vehicles, significant friction losses occur in the valve train, whereas in commercial vehicles using heavy diesel engines, friction in the valve train is not significant but most frictional losses occur in the piston assembly and bearing where rubbing surfaces are separated by an oil film. The viscosity grade of the engine lubricants has a profound effect on friction and fuel consumption, particularly in heavy-duty diesel engines. Higher viscosity oils provide adequate wear protection but create more resistance to motion and high frictional losses. Lower viscosity oils reduce frictional losses, but engine protection may be compromised, more so in high soot conditions unless the lube is formulated with the correct additive package. High temperature/high shear (HT/HS) viscosity is also important in achieving fuel economy and wear protection. In general, the lower the HT/HS rating, the better the fuel efficiency. However, too low an HT/HS rating can compromise wear protection. The level of fuel economy improvement when using lower viscosity lube depends on the engine design, operating condition, drive cycle, and fuel quality.

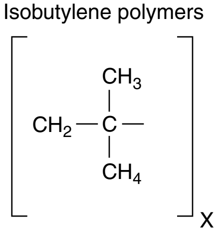
AUTOMOTIVE OIL ADDITIVES

Very little mineral lube oil without additives is sold in the market as a lubricant. Most commercial lubricants contain additives to enhance their performance, but the largest market for additives is in the transportation field, including engine and drive trains for cars, buses, trucks, locomotives, and ships. Motor oils, unlike many other industrial lubes, operate over a wide range of temperature under which they must provide engine lubrication, minimize engine wear, resist high-temperature lube degradation, and keep contaminants in suspension over a longer time interval. Generally, properties of the lube base stocks are not adequate to meet all these requirements; therefore many additives are added to the base stock to constitute a motor lube suitable for gasoline or diesel engines. On average, a typical motor oil may contain 18 percent additives and 82 percent base oil. Present-day petroleum-based motor oil may contain the following additives:

- Viscosity index improvers
- Detergents
- Dispersants
- Anti-wear/Extreme pressure additives
- Friction modifiers
- Antioxidants/Corrosion inhibitors
- Rust and corrosion control additives
- Pour point depressants
- Antifoam agents
- Other additives (seat swell agents/dyes/biocides, etc.)

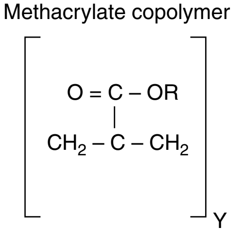
VISCOSITY INDEX IMPROVERS

The viscosity of lubricating oil changes with temperature. The rate of change depends on the composition of the oil. A naphthenic base oil viscosity changes more rapidly with a temperature increase compared with paraffinic base stocks. The viscosity of certain synthetic lubricants changes more slowly compared with paraffinic base oils. For a given oil, the viscosity index (VI) is a measure of change of viscosity with temperature. Thus a high VI implies a smaller change in viscosity with temperature, and a low VI implies large change in viscosity with temperature. The VI of a lubricating oil is of immense importance in applications where an appreciable change of temperature of the lubricating oil could adversely affect the startup or operating characteristics of automotive engines and other equipment. Lube manufacture aims at the highest possible VI so the change in viscosity of lube oil during actual use is minimal. The VI of an oil is estimated by the ASTM D 2270 test method. This method estimates the VI of a given oil based on its viscosities at 40 and 100°C. For an oil to be effective at low temperature and yet be thick enough to lubricate at high temperatures, oil must have a fairly flat viscositytemperature relationship. The change in viscosity of lube oil with temperature is defined by the VI of the oil. During the manufacture of petroleum lube base stocks, low VI components (aromatics) in the feed are either removed by solvent extraction or hydrogenated to naphthenes or paraffins to raise the VI of the lube. Raising the VI of lube beyond a limit by processing alone during base stock manufacture becomes uneconomical, and a further increase in VI is achieved by certain additives called VI improvers during motor oil formulation. VI improver additives make it possible to furnish multigrade oils commonly used in most engine oils today. These multigrade oils have a low-temperature viscosity equivalent to the first or a low viscosity number, but on heating they do not drop in viscosity as rapidly as straight mineral oils and have a viscosity of a higher grade at the elevated temperature. The improvement in the slope of the viscositytemperature curve is achieved by the addition of organic polymers. There are two main types of VI improvers: isobutylene polymers (Fig. 11-1) and methacrylate copolymers (Fig. 11-2). Molecular weight is chosen (typically weight average of 180,000 to 250,000). Typically the content of the VI improver in a finished motor lubricant may be between 0.5 and 10 percent by weight (wt %). High molecular


Isobutylene polymers

$$\left[CH_2-\overset{CH_3}{\underset{CH_4}{C}}- \right]_X$$

FIGURE 11-1 Lube additive.


Methacrylate copolymer

$$\left[CH_2-\overset{O=C-OR}{C}-CH_2 \right]_Y$$

FIGURE 11-2 Lube VI improver.

weight polymers give a higher VI improvement at a given concentration. With increasing molecular weight, polymers are increasingly subject to breakdown under shearing conditions encountered in high-speed rotating engine parts. The use of viscosity improvers makes it possible to meet both the low-temperature viscosity requirements of W grades as well as the high-temperature requirements of non-W grades. For example, the viscosity of 15 W 40 grade with a VI of 135 at a different temperature would be as follows:

Temperature ºC	Viscosity cP
–15	3000
40	105
100	14

Many of the organic polymers used as VI improvers are shear-sensitive compounds. This means that under high-shear conditions, there is change in the average molecular weight of the polymer and a reduction in its viscosity. The molecular weight change is believed to be due to the breakage of the chemical bond in the polymer chain. Of course this defeats the very purpose of adding these additives to the oil. Shear stability is a measure of the amount of viscosity an oil may lose during actual usage. Oil experiences very high stresses in certain areas of the engine such as in the oil pump, cam shaft area, piston rings, and in many areas where two mating metallic surfaces squeeze the oil film. As oil passes through these mating surfaces, a fraction of the polymer compound contained in VI additives, under severe mechanical stress, is permanently sheared or depolymerized. This results in a loss of viscosity of the oil and thus the effectiveness of the VI improver. The shear stability of an engine oil is measured by using the ASTM D 5275 test method. First, the viscosity of a formulated engine oil is measured. Next, the oil is exposed to severe shearing conditions by repeatedly pumping it through a specially sized diesel fuel injection nozzle at high pressure. After this operation, the viscosity of the oil is measured again. The percentage viscosity loss is measured by comparing the second viscosity measurement with the original viscosity. Although there are no specifications indicating required level of shear stability for engine oils, oils with lower viscosity loss would be preferable.

Shear Stability of VI Improvers

As stated earlier, many of the organic polymers used as VI improvers are shear-sensitive compounds. This means there is a change in the average molecular weight of the polymer and a reduction in viscosity every time the oil is subjected to high shear. Molecular weight change is brought about by breakage in the chemical bonds in the polymer chain, which defeat the very purpose of adding these additives to oil. It is essential that these compounds be sold in as stable condition as possible. In manufacturing these compounds, the mixture coming out of polymerization reactor may contain a wide variation of molecular weights and with a corresponding variation in resistance to shear. To overcome this problem, the polymer coming from the reactor is passed through a homogenizer. In the homogenizer, the polymer is subjected to an intense energy and shear environment, much more than what it is likely to undergo in the lube circuit of an engine. This ensures that a change in the viscosity of oil due to high shear in the engine is minimal. The product coming out of the homogenizer is remarkably stable with respect to viscosity change. The stability of the polymer additives in actual shear conditions encountered in engines is measured by the shear stability index (SSI),[1] which is defined in Fig. 11-3.

This index can be used to predict the viscosity of an oil after it has been used in an engine. Measurement of the shear stability index is done by the following procedure: The polymer additive is dissolved in oil and next heated from a minimum of 100 to 300°F, usually to 210°F to make it pumpable. The polymer solution is pumped to the homogenizer, which has special wearing parts. The solution is processed in one or more passes at a high homogenizing pressure. The pressure and number of passes used depends on the particular polymer and the desired viscosity reduction. The finished product is added to the oil to obtain the desired viscosity. The principal test is a viscosity

$$SSI = \frac{\mu_i - \mu_f}{\mu_i - \mu_0}$$

Where:

SSI = Shear stability index

μ_i = Initial viscosity in cSt at 100°C

μ_f = Final viscosity after subjection to high sheer, cSt at 100°C

μ_0 = Viscosity of base oil blend with all additives except VI improvers, at 100°C

FIGURE 11-3 Shear stability index.

check immediately after homogenization and again after 24 h of hold time to determine any viscosity regain if this occurs. The viscosity is usually determined at 210°F.

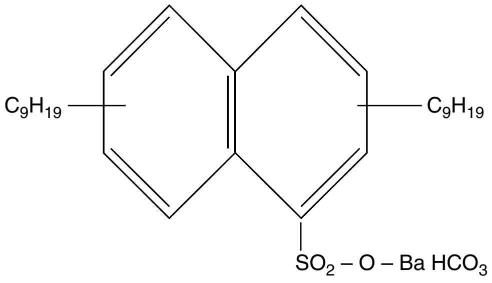
DETERGENT INHIBITORS

Lubricating oils for modern automotive engines are designed not only to provide adequate lubrication under varying temperatures and operating conditions, but also to keep the engine clean and provide protection against chemical corrosion from acidic combustion products. These important properties are added to it by means of alkaline reacting additives referred to as detergents/dispersants. During the combustion of fuel, sulfur is oxidized to SO_2 and SO_3. Part of these sulfur oxides combine with water during the combustion process and form sulfurous and sulfuric acid, which are very corrosive to engine components. To neutralize these acids, bases are needed. Thus oil-soluble bases must be present in the lubricating oils of internal combustion engines. Bases react with acids, sludge, and varnish precursors so as to neutralize them and keep them in solution. The compounds used for this service are generally metallorganic compounds such as sodium, magnesium or calcium sulfonates, salicyclates, phenates, thiophenates, and phosphonates. Oil-soluble bases such as calcium sulfonate and calcium phenates are also excellent deposit control additives.

Sulfonates

Sulfonates are the products of neutralization of sulfonic acid with a metallic base. Petroleum or natural sulfonates are a by-product of white oil manufacture. During white oil manufacture, lube base stock is treated with oleum. The sludge formed is separated by settling, oil is neutralized by an alkali, and then the sulfonates formed in the oil are extracted with a solvent like isopropyl alcohol. This process is repeated a number of times until the aromatics are completely removed. The structure of the organic petroleum sulfonate produced depends on the crude source and can be the aliphatic, naphthenic, or aromatic hydrocarbon group. Due to the high demand for natural petroleum sulfonates, sulfonates have become the main product and white oil the by-product. However, environmental concerns discourage the use of sulfuric acid, and white oil manufacturers are increasingly switching over to the hydrogenation route for white oil manufacture, resulting in a dwindling supply of natural sulfonates. Synthetic sulfonates are increasingly being manufactured by the reaction of alkylated aromatics of the proper molecular weight with sulfur dioxide. Metallic cations of sulfonate detergents are calcium, magnesium, and sodium. Oil-soluble sulfonates containing metals in excess of stoichiometric amounts are called basic sulfonates, and they are helpful in neutralizing acid bodies over a longer time interval apart from acting as dispersants of contaminants.

Preferred alkaline earth sulfonates are alkaline earth metal salts, preferably magnesium or calcium salts of an alkyl aromatic sulfonic acid with a molecular weight of 400 to 700 (Fig. 11-4). A finished lube may contain 2 to 5 percent by mass of these detergents.



Barium dionylaphthalene sulfonate

FIGURE 11-4 Structure of basic barium sulfonate, a metallic detergent.

Salicyclates

Salicylates are generally prepared from alkyl phenols by Kolbe's reaction. Here phenol is first converted into sodium phenoxide, by neutralization with sodium hydroxide. Next sodium phenoxide is heated with carbon dioxide under pressure. In this process a carboxyl group joins the ring next to the phenoxide group. Finally, this product is heated with dilute acid (e.g., hydrochloric acid) and 2-hydroxybenzoic acid is formed (Fig. 11-5). The salicylates of potassium, calcium, and magnesium are highly basic detergents that are used in diesel engine oil formulations.

$$C_6H_5OH + NaOH \longrightarrow C_6H_5O^- Na^+ + H_2O$$

$$C_6H_5O^- Na^+ + CO_2 \longrightarrow Na^{+-}O\ C_6H_4\ COOH$$

$$Na^{+-}O\ C_6H_4\ COOH + HCl \longrightarrow HO\ C_6H_4\ COOH + NaCl$$

FIGURE 11-5 Manufacture of salicyclates.

Phenates and Phenol Sulfide Salts

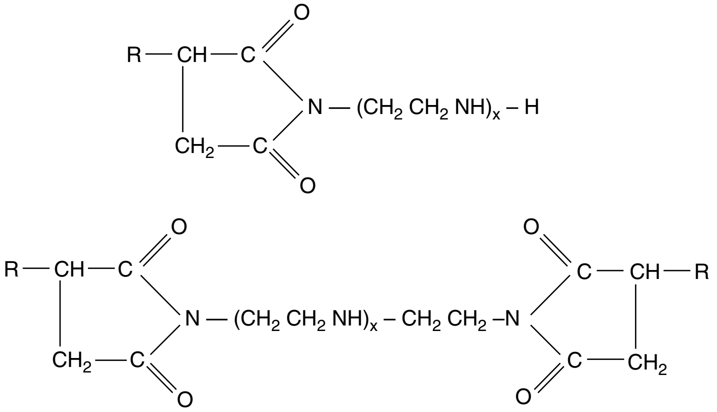
Metal phenates include salts of alkyl phenols, alkyl phenol sulfides, and alkyl phenol aldehydes. Oil solubility is provided by reacting or alkylating phenol with C_7+ olefins. Sulfur is incorporated into the phenate by reacting the alkyl phenol with sulfur chloride or elemental sulfur. The introduction of sulfur lowers the corrosivity of the product toward bearing metals and improves their antioxidant characteristics.

DISPERSANTS

The purpose of dispersants is to keep in suspension harmful products such as dirt, fuel, water, lube degradation products such as sludge, varnish, and oxidation products. Contaminants are bonded by polar attraction to dispersant molecules, preventing them from agglomerating. A major development in recent years has been the use of ashless dispersants. These materials may be categorized in two broad types; (1) high molecular weight polymeric dispersants used to formulate multigrade oils, and (2) lower molecular weight additives for use where viscosity modification is not necessary.

These additives are much more effective than the metallic type in controlling sludge and varnish deposits. The compounds useful for this service are again characterized by a polar group attached to a relatively long hydrocarbon chain. The polar group generally contains one or more elements: nitrogen, oxygen, or phosphorus. The solubilizing chains are generally higher in molecular weight than those in detergents. These ashless dispersants may serve the duel function of dispersants and viscosity modifiers. The preferred ashless dispersants are any type of polybutenyl succinimides. Specific examples of such dispersants are mono-type imides and bis-type imides (Fig. 11-6). Polybutenyl succinimides may be obtained by reacting polybutenyl succinate with maleic anhydride. These dispersants are added to lube to give a concentration of 0.1 to 0.2 percent in terms of nitrogen concentration based on total mass of the composition. Typical applications include diesel and gasoline engine oils, transmission fluids, power steering fluids, and some gear oils.

Polybutenyl succinimide type



Where:

R is polybutenyl group with mol weight between 1000 and 3000
and x is and integer between 2 and 5.

FIGURE 11-6 Structure of polybutenyl succinimide type ashless lube oil dispersant.

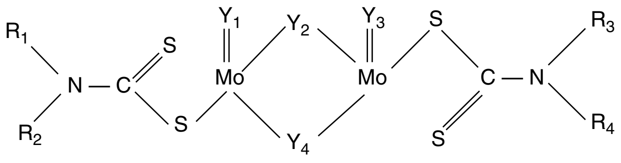
ANTI-WEAR/EXTREME PRESSURE ADDITIVES

Both anti-wear and extreme pressure (EP) additives reduce friction and wear and prevent scoring and seizure. The additives form a protective layer on metal parts by decomposition and adsorption. Anti-wear additives function in a moderate environment of temperature and pressure, whereas EP additives are effective under more severe operating conditions. Wear is the loss of metal with a subsequent change in clearance between surfaces moving relative to each other. If it continues, an attack of particulate matter and corrosive acids can occur at these points. Metal-to-metal contact is prevented by adding film-forming compounds that protect the surfaces either by physical adsorption or chemical reaction. Zinc dithiophosphates, organic phosphates, organic sulfur and chlorine compounds, sulfurized fats, sulfides and disulfide are used for this purpose, and these are very effective in reducing wear. Molybdenum disulfide and graphite additives are special forms of anti-wear additives known as anti-seize agents. They form a protective layer on metal parts by the deposition of molybdenum disulfide or graphite. Anti-seize agents work independently of temperature or pressure. The content in excess of the upper limit can accelerate the poisoning of the catalyst in an exhaust cleanup system, adversely affecting the cleanup of exhaust gases.

FRICTION MODIFIERS

Friction modifiers are lubricant additives blended in lube to reduce friction. Friction modifiers also reduce wear, scoring, and noise. Organic fatty acids and amides, lard oil, and high molecular weight organic phosphorus acid esters are used as friction modifiers. Molybdenum thiocarbamate (Fig. 11-7) is a popular friction modifier. It is added to lube formulation in a concentration of 0.02 to 0.06 percent by mass in terms of Mo concentration in many formulated lubes.

Friction modifier lube additive



Where:

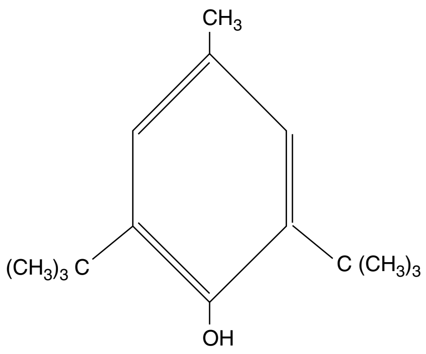
R_1, R_2, R_3, R_4 are same or different alkyl or aryl groups having 2 to 18 carbon atoms

Y_1, Y_2, Y_3, Y_4 are each independent sulfur or oxygen atoms

FIGURE 11-7 Structure of molybdenum dithiocarbamate.

OXIDATION INHIBITORS

The function of oxidation inhibitors is to retard the deterioration of lubricants associated with an oxygen attack. These additives act by either destroying free radicals (chain breaking) or reacting with peroxides involved in the oxidation mechanism. Among the most widely used antioxidants are phenolic type such as 2,6 ditertiary butyl phenol [$(C_4H_9)_2$ $C_6H_2(OH)]_2$ CH_2, 2,6-di tert-butyl para -cresol (BHT) etc.] (Fig. 11-8) and zinc dithiophosphates. The former are considered to be the



BHT (2, 6 DITERTIARY BUTYL 1-4-METHYL PHENOL)

FIGURE 11-8 Structure of antioxidant BHT.

chain-breaking type; the latter are of the peroxide-destroyer type. Oxidation inhibitors significantly reduce corrosion of bearing metal and lubricant oxidation by combustion products in the engine. Bearing corrosion is also reduced by detergents that neutralize the corrosive acids in combustion products. Certain anti-wear additives in lube such as zinc dithiophosphate, phosphosulfurized olefins, not only inhibit oxidation but also form a protective film on the bearing surface, making it impervious to acid attack.

RUST AND CORROSION INHIBITORS

Rust and corrosion are the result of attack on metal surfaces by oxygen and acidic products. The presence of water and impurities accelerates this attack. These additive work by neutralizing acids and forming protective films. Typical applications include engine oils, gear oils, metal working fluids, and greases. These inhibitors must work in lubricants and on surfaces above the liquid level. Vapor phase corrosion inhibitors (VPIs) provide a simple means of protecting internal components against rust in gear boxes, engines, and other closed surfaces. VPIs fill the closed spaces with vapor that forms a monomolecular protective layer on all metal surfaces. Contrary to what the name suggests, VPIs actually have low vapor pressure and are solids or liquids at room temperature. The most common form of VPI is a salt of an amine and a weak acid. An example is carbonate of dicyclohexyl amine. This VPI, in actual usage, dissociates to an amine and an acid that recombine on metal surfaces.

POUR POINT DEPRESSANTS

Pour point depressant additives prevent the congealing of oil at low temperatures. The phenomenon is associated with the crystallization of paraffin wax, which is present in lube base oils. To provide a low pour point of the finished lube, wax is removed from the feed during manufacture of lube base stock, by a solvent dewaxing or catalytic dewaxing process. Complete dewaxing would reduce the yield of base stock to uneconomic levels, however; therefore certain additives are used that lower the pour point of the lube oil by retarding the growth of wax crystals and thus keep the oil pumpable. In cases where VI improvers such as polymethacrylates are added during lube formulation, supplemental pour point depressants are not required.

ANTIFOAMANT ADDITIVES

Almost all lubricants tend to foam due to the agitation and aeration that occurs during lube usage. Air entrainment due to agitation increases foaming. The presence of detergent and dispersant additives also encourages foaming. Foaming promotes oxidation and reduces the flow of oil to machines. Antifoam agents are added to reduce foaming. These additives act by reducing surface tension, which speeds up the collapse of foam. Antifoamants are added typically in a concentration of 0.0005 to 0.001 percent by weight of the total lube. The chemicals used are silicone polymers (polymethylsiloxanes; viscosity 95,000 to 105,000 cSt at 77°F).

OTHER ADDITIVES

In addition to the major types of additives already discussed, minor amounts of some other additives are added to automotive and industrial lubricant to serve a specific purpose. For example, dyes are added to mark lubricant types and seat swell agents are added to counteract the adverse effect of additives on seals. Seal swell agents react with elastomer to cause seal swell. Organic phosphates and aromatic hydrocarbons are used for this purpose. Metal deactivators reduce the catalytic effect of metals on oxidation rates. These act by forming an inactive film on metal surfaces by complexing with metal ions. Organic complexes containing nitrogen, sulfur, amines, sulfides, and phosphites are used. Biocides are sometimes added to bulk storage tanks to retard or prevent bacterial growth. Usually additive manufacturers present an additive package that is added to base oil to formulate a lubricating oil for a specific use. Additive package suppliers usually have their package tested and approved with a base stock. Additive package may include detergents, dispersants, oxidation inhibitors, antifoamants.

Additive manufacturers recommend the dosage of the additive package to be added and the type of base stock to be used for lube blending. Additive package and base oil can present compatibility problems if the base oil is not of the recommended type. Keeping additives in suspension in base oil can present a challenge. Aromatics in base stocks that provide solubility to additives can be quite low. Additive package manufacturers also provide the chemical analysis (metals, sulfur, nitrogen, TBN, estimated sulfated ash) and physical properties of additive package (specific gravity, viscosities at 40 and 100°C), and maximum handling and storage temperatures. Some additional additives such as VI improvers, dyes, not present in the package but required to meet requirements, may also be included. Additive manufacturers usually have different additive packages for, say, medium-speed diesel engines, railroad diesel engines, marine diesel engines, gasoline engines, gear oils, automatic transmission fluids, and so on, tested with different types of base stocks and end uses that make lube formulation easier.

ADDITIVE DEPLETION

The principal conditions that cause depletion of these additives in lubricating oils are described in the following paragraphs.

Oxidation

Oxidation occurs when the hydrocarbon constituents of lube oil combine chemically with oxygen. Oil in the engine will combine chemically with available oxygen under certain conditions to form a wide variety of oxidation products. Many of these direct oxidation products combine with other materials such as wear metals, solid contaminants, and moisture to form corrosion products. Oil oxidation is accelerated by heat and pressure. Various studies have shown that lube oil oxidation rate is doubled for every 15 to 20°F increase in temperature. Also, engine load that dictates the level of oxygen intake can cause accelerated acid formation, corrosion, oil thickening, deposit formation and accelerated wear.

Nitration

The combustion chamber of the engine provides one of the few environments where there is sufficient heat and pressure for reaction of atmospheric nitrogen in engine intake air with oxygen to form nitrogen oxides. These nitrogen oxide products enter the lube oil through normal blow-by, which reacts with the moisture present in the lube to form a corrosive and powerful oxidant, nitric acid, which rapidly accelerates the oxidation rate of the oil. “Blow By” is escape of compressions and combustions gases past piston and piston rings into the crank case.

Acid Formation

Acids are formed in the lube by several sources. In all forms of fuels used in internal combustion engines, varying amounts of sulfur are present. Sulfuric acid is formed when sulfur molecules react with oxygen in the combustion chamber to form sulfur oxides. These sulfur oxide molecules are blown past the rings and enter the oil. Here the sulfur oxide molecules mix with moisture to form highly corrosive sulfuric acid.

Soot Contamination

One of the major contaminants facing new lube oils today is soot contamination, which is particularly severe in diesel engines. Most of the carbon soot particles generated within the engine are 10 microns or smaller. Engine full-flow filters are designed to remove only 15-micron particles and larger. Thus these filters do little to remove soot contamination. A diesel engine oil used in trucks may last 12,500 miles, burning 1800 gal of fuel at 7 miles per gallon. During this 12,500-mile journey, more than half a pound of soot will enter the oil. Soot will enter the lubricating oil at the rate of 0.0048 ounce for every gallon of diesel burned. In recent years, engine manufacturers have developed new engine designs to meet the new environmental emission standards requiring lower emission of nitrogen oxides and particulate matter. In these new (exhaust gas recirculation, or EGR, type) diesel engines, exhaust gas from the engine is cooled and recirculated through the engine to reduce oxygen concentration within the cylinder, thereby lowering the flame temperature and the formation of nitrogen oxides (NOx). These newer engines emit fewer contaminants, including carbon soot due to exhaust gas recirculation, and therefore higher soot levels are being found in engine oils. Thus the incorporation of EGR technology has resulted in a shorter drain interval for lube oils in diesel engines.

ENGINE OIL FORMULATION

The crankcase oil used in engines is a formulated product consisting of a base oil in which various additives are dissolved. In an engine oil, the base oil components may be 75 to 85 percent of the total formulated lube, and the remaining 15 to 25 percent may be different types of additives. Viscosity modifiers and detergent inhibitors are the most prominent additives. Other additives used in lube formulation are dispersants, AW/EP agents, oxidation inhibitors, antifoamants, rust inhibitors, and demulsifiers. Base oils of a required viscosity are obtained by blending different base stocks such as neutrals and bright stocks. Table 11-4 shows the typical concentration of base oil and various

TABLE 11-4 Automotive Lube Oil Composition

	Range % wt	Typical
Base oil	75–85	
Additives	15–25	
Total	100	
Detergents	1.5–5	Alkaline earth (ca/mg) metal sulfonate, MW 400–700
Dispersants (polybutenyl succinimide)	0.05–0.2*	Polybutenyl succinimide
VI improver	0.5–10	Polymethaacrylate, MW 180,000–25,000
Friction modifier	0.04–0.15†	Molybdenum thiocarbamate
Wear inhibitor	0.04–0.09‡	Dialkyldithio zinc phosphate
Anticorrosion		
Oxidation inhibitors	0.3–2.0	Phenolic oxidation inhibitors such as 2,6 ditertiary butyl phenol
Antofoamants	0.0005	
Pour point depressant		
Metal deactivators	0.005	

*In terms of nitrogen concentration in finished lube.
†Molybdenum concentration in total finished lube.
‡In terms of zinc concentration in finished lube.

TABLE 11-5 Commercial Lubricating Oil Characteristics

SAE viscosity grade		15W–40	10W–30
API service classification	Diesel Gasoline	CH-4, CG-4, CF-4, CF-2, CF SJ	CG-4, CF-4, CF SH
API gravity		27.9	28.9
Specific gravity		0.8877	0.8822
Flash point	ºC	218	210
Pour point	ºC	–33	–33
Viscosity at ºC			
–15	cP	3000	
–20	cP		2840
–25	cP	25,000	
–30	cP		19,500
40	cSt	120.7	73
100	cSt	15.5	11.0
High-temperature/high-shear viscosity	cP, 150ºC	4.4	3.4
Viscosity index		134	141
Zinc	Wt %	0.142	0.142
Nitrogen	Wt %	0.124	0.113
Sulfate ash	Wt %	1.4	1.4
TBN	mg KOH/g	12.2	11.8

additives in automotive engine oils for gasoline and diesel engines. Properties of lube oils 15W-40 and 10W-30 are shown in Table 11-5. Properties of a few other commercial engine oils are shown in Table 11-6.

The additives are added to the base oil to enhance its performance when used in various types of engines. The most important properties of a lubricating oil are its viscosity and alkali reserve (base

TABLE 11-6 Typical Properties of Commercial Motor Oils

	1	2	3	4	5
SAE grade 20W–50					
Viscosity index	122	119	155	121	130
Flash point, °F	440	419	430	432	450
Pour point, °F	–15	–13	–25	–11	–15
Sulfated ash, Wt %	0.85	0.7	0.9	0.74	1
Zinc, Wt %	0.12	0.11	0.15	0.12	0.15
SAE grade 15W–40					
Viscosity index	134	136	135	146	140
Flash point, °F	415	421	399	410	420
Pour point, °F	–15	–27	–11	–25	–10
Sulfated ash, Wt %	1.3	1	0.9	1	0.99
Zinc, Wt %	0.14		0.14	0.13	0.13
SAE grade 15W–30					
Viscosity index	140	150	133	155	130
Flash point, °F	415	401	400	405	410
Pour point, °F	–33	–26	–31	–35	–26
Sulfated ash, Wt %	0.85	0.96	0.85	1	1.2
Zinc, Wt %	0.12	0.11	0.13	0.15	0.2

TABLE 11-7 Lubricating Oil Base Number (BN)

Natural gas operation of spark-ignited (SG) and dual-fuel (DF) engines	
BN 4–7	For use in gas engines
LFO operation of dual-fuel (DF) engines	
BN 12–15	For use in dual fuel engines using light fuel oil
HFO operation of DF engines	
BN 30–55	For use in DF using heavy fuel oils
Diesel engines	
LFO operation	
BN 12–15	For low-sulfur diesel fuel
BN 20–30	For high-sulfur diesel fuels
HFO operation	
BN 30	Share is continuously decreasing. Can be used with low SLOC or when engine is equipped with SCR catalyst
BN 50–55	When engine is equipped with wet lube oil sump and fuel sulfur content is above 2% or more

number, or BN). In addition, many other properties of the oil affect the performance of the engine. Fuel quality significantly affects the kind of lubricating oil to be used. For example, for a low-sulfur fuel such as natural gas, little sulfur dioxide is formed during combustion. In this case a lubricating oil with a low BN, 4 to 7, may be OK. In case the fuel contains high sulfur, 0.5 to 5 percent, a higher alkali reserve is required to prevent corrosion damage. For fuels containing 2 percent or more sulfur, a high BN (50 to 55) lubricating oil gives longer lube oil change intervals compared to lower detergency levels (BN) lubes. Initial cost of the lube may be higher, but overall economics dictates their use. BN values for some diesel and gasoline engines are shown in Table 11-7. After an engine has run certain number of miles; typically 5000 to 10,000, the engine oil is drained and new oil is filled in its place. The reason is that although the base oil remains broadly unchanged, the additives within the oil get depleted during actual engine running because of contaminants, acids, corrosion, and wear products formed in the oil. Lubricating oil ages and undergoes degradation during operation and certain additives are partly consumed. For these reasons, condemning limits have been set for various physical and chemical properties of lubricating oils. Table 11-8 presents the typical condemning

TABLE 11-8 Condemning Limits for Used Lubricating Oils

Property	Units	Condemning limits, gas engines	Condemning limits, medium-speed diesel engines	Test method
Viscosity	cSt, 100ºC	–20%/+25%	–20%/+25%	ASTM D 445
Viscosity	cSt, 40ºC	–25%/+50%	–25%/+45%	ASTM D 445
Water	Vol % mass, Max.	0.3	0.3	ASTM D 95/D 1744
Base number	mg KOH/g, Max. depletion	50%	20%/50%*	ASTM D 2896
Total acid number	mg KOH/g, Max. increase	2.50%		ASTM D 664
n-Pentane insoluble	Wt %, Max.	1.00%	2.00%	ASTM D 893b
Flash point	PMCC, ºC Min.		170	ASTM D 93

*Max. 50% depletion for LFO operation and max. 20% depletion for HFO operation.

limits for used lube oils in gas and diesel engines. The high water content can be reduced by efficient centrifuging, which can extend the life of lubricating oil.

Lube formulators are faced with conflicting demands from customers, original equipment manufacturers (OEMs), emission standards set by government agencies, lube manufacturers' profitability, and the marketability of formulated lube. Customers demand increased oil drain intervals (50,000+ miles), improved fuel economy, longer engine life, and meeting these requirements increase the cost of production.

OEMs desire enhanced engine protection from viscosity increase and soot, low volatility, greater oxidation stability, corrosion protection, and enhanced low temperature performance.

Environmental agencies all over the world are targeting emissions from internal combustion engines, particularly nitrogen oxides (NOx standards per g/BHP/h) and particulate matter from engines (g/BHP/h), are constantly decreasing compared with the engines of the 1990s.

EFFECT OF BASE STOCK QUALITY

Optimal engine oil performance requires proper balance of lube base stock characteristics and additive technology. Paraffinic base stocks are preferentially used to formulate most of the world's automotive and industrial lubricants, including engine oils, transmission fluid, and gear oils due to their better oxidation stability, higher viscosity index, and lower volatility relative to their comparable viscosity grades of naphthenic base oils. Naphthenic base oils have a lower pour point and better solvency characteristics compared to paraffinic base oils, which make them particularly useful in formulating low-temperature hydraulic oils, refrigeration oils, rubber process oils, metal working oils, cylinder lubricants for large engines, and greases. The possibility of longer life automobile engine oils has emerged over the past few decades with availability of polyalphaolefin (PAO) synthetic lubes. These oils came with 25,000 miles+ suggested oil change intervals. Nevertheless, the high cost of PAO base stocks limited their market share. Hydrocracked and hydrotreated lube base stocks constituting group II and group III lubes have very high saturates and very low aromatics. Absence of aromatics make them more resistant to oxidation and thus minimizes sludge and varnish deposits. The service life of oils blended with group II and III base stocks, with VI of 120 or more is estimated to be double or more compared with oils of group I base stocks.

However, despite the advantages of group II and group III base oils, their use in motor oil blending is not without problems, a few disadvantages are:

- Automobile engine oils are blended with a large amount of detergents, oxidation inhibitors, antiwear, and many other additives. In the absence of aromatics in group II and group III base stocks, additive solubility in the base stocks is very poor and the additives tend to separate from base oil. To avoid such a possibility, blending either with group I solvent refined oil or with synthetic ester fluid may be required, thus sacrificing potential longer life. Altered solvency action with paraffinic hydrocracked base oils may adversely affect some gaskets, seals' paint, and coupling components in existing engines.
- Due to cracking, viscosity of lube base stocks produced by hydrocracking is limited. Hydrocracking of aromatic and cycloparaffin molecules results in a severe reduction in viscosity. Hydrocracked base stocks have a maximum viscosity of 320 to 460 cSt at 100°F. Higher viscosity grades are required for certain industrial gearing, large reciprocating compressors, and many other applications. Group III base stocks consisting mainly of paraffins have still lower viscosity, which restricts their usage to 0W and 5W SAE grades. For blending higher viscosity grades, more viscous bright stock from traditional lube making, synthetic polyalphaolefins, or long chain polymeric material must be used.

AMERICAN PETROLEUM INSTITUTE SERVICE CLASSIFICATION

The American Petroleum Institute (API) service classification of motor oils is based on the performance of an oil in certain types of engines. Whereas the SAE classification refers only to oil viscosities at specified temperatures, API specifications refer to oxidation protection, high temperature engine deposits, acid formation, foaming, sludge control, engine emissions, and other properties critical to engine performance, pollution control, and oil consumption. API maintains a system of service classification ("S" rating) for gasoline engines and commercial classification ("C" ratings) for diesel engines. Changes are made to the specifications in consultation with major automotive companies, original equipment manufacturers, oil refining companies, and engineering companies directly involved in automobile manufacture. Periodic changes are made to the specifications to keep them updated with current gasoline and diesel engine technology, refining processes, and emission norms. It may be noted that when a new specification is released, it makes the previous specification obsolete.

Specification revision are driven by the following objectives: General oil improvement includes lower oil volatility and reduced additive depletion. Lower volatility reduces oil consumption rates and piston deposits and help keep viscosity from rising over service life. Reduced additive depletion ensures adequate protection over the course of oils service life.

Rapidly changing emission standards have led to stringent lubricant requirements. Specifications are changing every two or three years. The OEM demand lubes with greater protection from soot-aggravated wear and viscosity increase, reduced consumption, lower volatility, greater oxidative stability, material compatibility, and corrosion protection. The API administers the licensing and certification of engine oils in the United States.

API service classification is listed on each container of lubricating oil sold in the market or at service stations in the United States, and it is easy to match it with the recommended oil as per its service manual. The API system has two general classifications:

- First letter "S' indicates that oil is appropriate for "spark-ignited" or gasoline engines (typical passenger cars and light trucks).
- First letter "C" indicates that oil is appropriate for "compression-ignited" or diesel engines.
- The second letter in each category indicates the performance level of the category. For "S" categories, the performance level increases as the categories go through the alphabet. However, the same is not true for the "C" categories because the types and the intended application range of diesel engines is very great. It is important to refer to the service manual of the engine for appropriate performance recommendations.

GEAR OILS

Gear oils are heavy high-viscosity lubricating oils that are used in enclosed units containing gears. Gear oils perform a number of functions. These oils reduce friction and wear, act as heat transfer agents, and protect against corrosion and rust. They contain additives to minimize oil oxidation, inhibit foaming, and separate water readily. Gear lubricants SAE viscosity grades should not be confused with engine oil SAE viscosity grades. A gear lubricant and an engine oil having the same viscosity will have widely different SAE viscosity grade designations as defined by two viscosity classifications.

Viscosity is the most important property of gear oils. The viscosity of oil should be high enough to protect the gear teeth against direct metal-to-metal contact. High VI is also important. The oil should be able to provide a consistent lubricating film over the operating range of the gear box. Enclosed high-speed gears are formulated with rust and oxidation inhibitors and anti-wear agents. Worm gears are blended with synthetic fatty oils to provide lubricity for sliding motion under heavy pressure. Open gear sets require high-viscosity base oils with extreme pressure and anti-wear additives.

SAE GEAR OIL CLASSIFICATION

Table 11-9 shows U.S. standard SAE J306 (July 1998) for automotive gear lubricants, based on viscosity. Note that viscosities at 100°C range from 4.1 to 41 cSt; crankcase oil viscosities range from 3.8 to 21.9 cSt. Another important classification is the American Gear Manufacturers Association (AGMA) (Table 11-10), which has set up a numbering system to define gear oil viscosities. Wide-span multigrade oils are becoming more and more popular due to their fuel economy and applicability over a wider ambient temperature range. Multigrades like 75W-90, 80W-90, and 85W-140 are gaining in importance in areas with wide swings in ambient temperatures. One problem with many traditional gear lubes is that lubes do not stay in grade after being in use for some time, due to a loss in viscosity.

TABLE 11-9 Viscosity Classification for Axle and Manual Transmission Lubricants

Viscosity classification: SAE J306

SAE viscosity number	Maximum temperature for viscosity of 150,000 cP ºF	Maximum temperature for viscosity of 150,000 cP ºC	Viscosity at 210 ºF minimum		Viscosity at 210 ºF maximum	
			cSt	SUS	cSt	SUS
70 W	–67	–55	4.1			
75	–40	–40	4.2	40		
80 W	–15	–26	7.0	49		
85 W	10	–12	11.0	63		
80			7.0		<11	
85			11.0		<13.5	
90			14.0	74	<25	120
140			25.0	120	<43	200
250			43.0	200		

TABLE 11-10 AGMA Gear Oil Standards (AGMA-9005-E02)

AGMA no. lubricant	Equivalent ISO grade	Viscosity range cSt, 40ºC	Viscosity range SUS, 40ºF
1	46	41.4–50.6	193–235
2	68	61.2–74.8	284–347
3	100	90–110	417–510
4	150	135–165	626–765
5	220	198–242	918–1122
6	320	288–352	1335–1632
7	460	414–506	1919–2346
8	680	612–748	2837–3467
8A	1000	900–1100	4121–5098

The shear stability requirement test in SAE standards assures that the lubricant stays within the acceptable range of each viscosity grade. Formulation of gear oil is done with more shear-stable VI improvers or different or synthetic base stocks to stay in grade. Synthetic gear oils are used in many industries. Synthetic gear oils are known to prevent startup engine wear better and are pumped to critical surfaces much faster than mineral oils. Table 11-11 lists the properties of some commercial synthetic gear oils.

TABLE 11-11 Properties of Synthetic Gear Oils Commercial Grades

	1	2	3	4
Base oil	PAG	PAG	PAG	PAG
Density, 60ºF, kg/M^3	1074	1072	1051	1070
Kinematic viscosity, 40ºC, cSt	222	460	680	1000
Kinematic viscosity, 100ºC, cSt	34.4	73.2	114	160
Viscosity index	203	239	276	286
Pour point, ºF	–27	–33	–4	–4
Flash point, COC, ºF	568	586	509	509

AUTOMOTIVE LUBRICANTS TEST METHODS

Thin Film Oxygen Uptake

The thin film oxygen uptake (ASTM D 4742) evaluates the oxidation stability of lubricating oils. A mixture of test oil and fuel found in gasoline engine operation (oxidized/nitrated fuel, soluble metals, and distilled water) are placed in a test vessel, which is pressurized with oxygen and placed in a heated bath. Antioxidant breakdown is evident when the oxygen pressure in the vessel rapidly decreases. At this time the induction time (breakpoint) of oil is recorded.

A good quality oil may have an induction time in the order of 500 min. Superior oxidation stability of motor oil allow it to effectively resist the formation of engine deposit and sludge, keeping the engine running clean and extending the oil life. It also resists thickening, maintaining its superior wear protection and lubrication properties and maximizing fuel efficiency.

High-Temperature/High-Shear Test (ASTM D 4683)

The high-temperature/high-shear test measures the lubricant viscosity under severe high-temperature and shear conditions that resemble highly loaded journal bearing in fired internal combustion engines. In order to prevent bearing wear, it is important for a lubricant to maintain its protective viscosity under severe operating conditions. The minimum high-temperature/high-shear viscosity at 150°C for SAE-30 oil is 2.9 cP. The superior viscosity retention of a good quality oil in the face of severe temperatures and shear conditions allows it to provide continuous unsurpassed protection for engine bearings, extending equipment life and preventing wear.

Noack Volatility Test (ASTM D 5800)

The Noack volatility test determines the evaporation loss of lubricant in high-temperature service. The more the motor oil vaporizes, the thicker and heavier the remaining oil becomes, contributing to poor circulation, reduced fuel economy and increased oil consumption, wear, and emissions. Generally a maximum of 15 percent evaporation loss is allowable in motor oils. Low volatility of a well-formulated oil allows it to maintain its superior protective and performance qualities throughout extended drain intervals even under severe operating temperatures. In addition, oil consumption and emission are minimized and fuel economy is maximized.

Pour Point (ASTM D 97)

The pour point determines the lowest temperature at which lubricant will flow when cooled under prescribed conditions; the lower the lubricant's pour point, the better protection it provides in low-temperature service.

The low pour point of an oil allows it to maintain its fluidity in low ambient temperatures, reducing drag on moving vehicle parts, providing critical engine components with quick, essential lubrication, and easing startup in cold temperatures. Wear is greatly reduced and equipment life is extended.

Total Base Number (ASTM D 2896)

New and used lubricating oils generally contain basic constituents such as sulfonates, phenates, salicyclates, and so on, of alkaline earth metals (e.g., calcium, magnesium) to impart alkalinity to lube formulations. BN is a measure of the amount of basic substance in oil. It is equal to the quantity of perchloric acid equivalent to the number of milligrams of potassium hydroxide required to titrate 1 g of sample. In the test, the sample is dissolved in a mixture of chlorobenzene and glacial acetic acid and titrated with perchloric acid ($HClO_4$) in glacial acidic acid with a potentiometric titrimeter.

TBN is the measurement of a lubricant reserve alkalinity that aids in the control of acids formed during the combustion process. The higher the motor oil's TBN, the more effective it is in suspending wear-causing contaminants and reducing the corrosive effect of acids over an extended period of time. The high TBN of an oil provides superior protection and performance over extended drain intervals.

High TBNs are essential to control deposits in four-stroke cycle diesel engines and to neutralize the effect of high-sulfur fuel. Engine burning fuel with more than 3.5 % sulfur requires an engine oil with high TBN of 30–50 whereas engine burning low sulfur fuels, with less than 0.5 % sulfur require a low TBN (6–10) oil.

Sulfated Ash Content

Sulfated ash is the noncombustible residue of a lubricating oil according to ASTM D 582 and D 874. Sulfated ash is thus the solid material left when the oil burns. A high sulfated ash content tends to form more sludge and deposits in engine, which may cause valve failure under certain operating conditions. Because most detergents are metallic compounds, the percentage of sulfated ash has been considered to have a relationship to detergency. As TBN increases, sulfated ash also increases. Thus a motor lubricant with a TBN of 10 or more is most likely to have sulfated ash of more than 1 percent. Lubricating oil with a low sulfated ash content is more appropriate. In the ASTM D 874 test method, the sample is ignited and burned until only ash remains. After cooling, the residue is treated with sulfuric acid and heated at 775°C until oxidation of the carbon is complete. The ash is then cooled, retreated with sulfuric acid, and heated at 775°C to a constant weight. Sulfated ash is used to indicate the concentration of known metal-containing additives in new oils. When phosphorus is absent, Ba, Ca, Mg, Na, and K are converted to their sulfates while tin and zinc are converted to their oxides, but when phosphorus is present with metals, it remains partially or wholly in sulfated ash as metal phosphates. Sulfur and chlorine do not interfere in the test.

Zinc Content

Of great importance in engine lubrication are zinc compounds such as dialkyl-dithio zinc phosphates, used in lubricating oils as an extreme pressure/anti-wear and antioxidant additive. Zinc is only used when there is actual metal-to-metal contact in the engine. Under normal engine operations, lube oil film prevents any metal-to-metal contact; however, under certain abnormal operating conditions (high engine loads, high temperatures, etc.) if metal-to-metal contact occurs, zinc compounds react with metal or get adsorbed on the surface to form a film that prevents scuffing and wear. Typically a level of 0.11 percent zinc is sufficient to protect an automobile engine for extended oil drain interval under normal usage. For air-cooled motorcycles or turbocharged cars, higher zinc is sometimes allowed to give protection for a longer time. Generally, more zinc may lead to more deposit formation and plug fouling.

COLD CRANK SIMULATOR (ASTM D 5293)

The cold crank simulator test determines the apparent viscosity of lubricants at low temperatures and under high shear rates. Viscosity of lubricants under these conditions is directly related to engine cranking and startability. The lower the lubricant's cold cranking viscosity, the easier for an engine to turn over cold ambient conditions. For example, 10 W motor oils are tested at –25°C and must have a viscosity below 7000 cP to pass SAE J300 specifications.

The low cranking viscosity of an oil reduces drag on moving engine parts and allows the engine to achieve a critical cranking speed in extremely low temperatures. Engines turn over quickly, and dependability in cold winter temperatures increases.

Cold Temperature Starting

To start effectively, the engine must reach a critical cranking speed. As the temperature drops, achieving critical cranking speed becomes more of a challenge. Low temperatures cause motor oils to thicken. If they thicken too much and impose excessive drag on the moving parts, critical cranking speed will not be achieved and the engine will fail. Motor oils used in cold climates must maintain a sufficient low cranking viscosity to allow engine turnover at the lowest temperatures. If the motor oil is able to meet this challenge of allowing the engine to turn over, it immediately faces another significant challenge of providing quick, critical lubrication to the engine-bearing and other moving parts. Two types of engine pumping failure can result from cold thickened motor oil: air binding failure and flow limited failure. Air binding failure occurs when motor oil surrounding the pump inlet screen gets sucked into the pump but is not replaced by new oil from the sump. The oil pump inlet screen then gets starved for fluid and the oil pressure becomes erratic as air is entrained and proper oil flow cannot be maintained. Flow limited failure occurs when oil becomes so thick that it cannot be pumped through the narrow passages that deliver oil to the engine moving parts. All motor oils thicken in cold temperatures but how much they thicken is significant to the level of protection an engine receives.

Pour point tests (ASTM D 97) pinpoint the temperature at which a motor oil thickens to the point it cannot flow. When the oil stops flowing, it is useless. For an engine to receive even minimal protection, it is important that it has a pour point lower than typical winter minimal temperatures. Petroleum-based motor oils face significant challenges at low temperatures because paraffinic wax begins to crystallize as the temperature drops. These wax crystals agglomerate into larger structures and the motor oil gels and fail to flow, starving the engine of vital lubrication. To hinder the growth of wax crystals, additives known as pour point depressants are added that lower the pour point. Petroleum-based lube base oils may have a pour point of 5°F, but pour point additives can lower it by another 25°F.

FOUR-BALL WEAR TEST (ASTM D 4172)

The four-ball wear test determines the wear protection properties of a lubricant. Three metal balls are clamped together and covered with test lubricants while a rotating fourth ball is pressed against them in sliding contact. This contact rapidly produces a wear scar. The smaller the average wear scar, the better the wear protection provided by the lubricant. A good quality motor oil must provide protection against engine wear. Thus equipment life is extended[2] and repairs, downtime, and expenses are reduced.

REFERENCES

1. Rohm and Hass Company, Philadelphia, PA, "Acryloid 700 series."
2. M. Khonsari, "New Lubes Last Longer," *Machinery Lubrication Magazine,* May 2004.