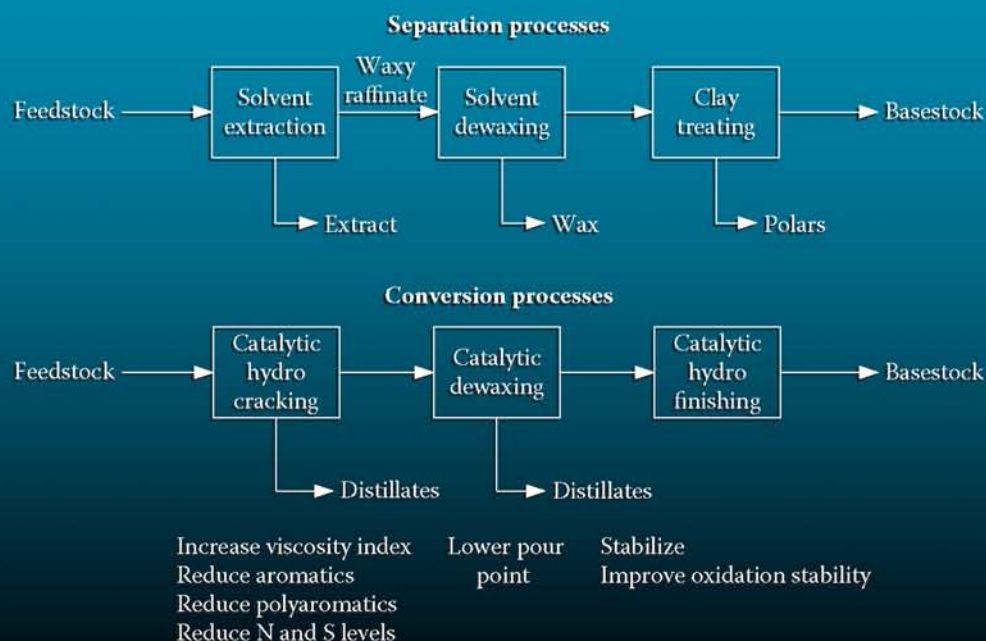


# Process Chemistry of Lubricant Base Stocks



Thomas R. Lynch

# **Process Chemistry of Lubricant Base Stocks**

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Thomas R. Lynch

*Mississauga, Ontario, Canada*



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# Preface

The purpose of this book is to provide the reader with an introduction to the chemistry of lubricant base stock manufacturing processes which use petroleum as feedstock and to the development work that has gone into this area over the past century and a half. I believe there is a need for such a work and it should appeal to those involved in either process or product development. The reader will gain insight into the chemical techniques employed and an introduction to many of the most significant papers in this area.

The unifying thread here is the chemistry of the process steps and therefore the structure, reactivity, and physical properties of the compounds existing naturally in petroleum and their subsequent transformation. The connections between structure, physical properties, and reactivity have been unraveled over time through rigorous investigations from both industry and academia. The revolutionary changes which the industry has seen over the past 25 years have truly been remarkable and are a tribute to the many people involved in the petroleum, lubricants, and automotive industries. In this book I have not sought to be comprehensive, rather to introduce the main chemical concepts and provide the reader with the most important sources for the background of the chemistry involved.

Early chapters provide a background to some of the physical properties that base stocks are expected to meet, the chemical and physical means by which they are distinguished, and the relationships between structure and physical properties. The viscosity index property is a key measure of viscosity response to temperature and deserves the attention of the full chapter (Chapter 3) that it receives. Methodology to determine both petroleum and base stock composition would require several books to outline. I have chosen to restrict this subject in Chapter 4 to a number of older methods which are still applicable but I have also included some discussion of NMR methods which increasingly will play a vital role. Since oxidation during use is probably the biggest hurdle that lubricants face, Chapter 5 provides a summary of the most significant work on the oxidation of base stocks and those oxidation studies on formulated products that reflect information on base stock composition and the process.

At this stage, having outlined the trends in desirable chemical structures and properties of base stocks, subsequent chapters deal with the commercial processes that have emerged, still paying close attention to the changes at the molecular level. The separation processes of solvent extraction and solvent dewaxing are outlined in Chapter 6 together with some description of the results from a very fine study by Imperial Oil people on the chemistry of hydrofinishing, a new technology at the time which rapidly displaced clay treating. Chapter 7 provides an account of the development of hydrocracking as a lubes process, which has



come to dominate base stock manufacturing in North America, now widespread throughout the world, and made possible Group II and III base stocks. In Chapter 8, I have attempted to provide a detailed account of the chemical changes due to hydroprocessing, the equilibria, rates, products and impact on physical properties. Chapters 9 and 10 focus on the important art of dewaxing by processes other than solvent dewaxing; by wax removal through formation of urea clathrates, by cracking via “cat dewaxing” or through the remarkable development of wax hydroisomerization by Chevron’s Isodewaxing<sup>TM</sup> process or that of ExxonMobil’s MSDW<sup>TM</sup> process.

The penultimate chapter is on the production of White Oils, where the processes have close links to those of base stocks, and the last chapter, departing from petroleum-sourced base stocks, is focused on the processes involved in the production of highly paraffinic (and very high quality) base stocks from natural gas. This is the potential elephant in the base stock world because of anticipated quality and volumes.

My thanks go to my former colleagues at Petro-Canada from whom I learned so much, colleagues, particularly Mike Rusynyk, who assisted in this book’s preparation by reading and commenting on parts of this work, to publishers, companies and authors who gave permission to reproduce figures and tables, and to my editor at CRC Press, Jill Jurgensen, who patiently dealt with all my questions.

My final thanks go to my wife who has waited patiently for this to come to an end.

---

# Author

**Tom Lynch** is an independent consultant in the lubricants industry. He has 25 years of experience with hydroprocessed lubes working for Petro-Canada in its Research and Development Department on Process Development and subsequently at the company's Lubricants Refinery. He obtained his B.Sc. degree from University College, Dublin, Ireland, and his Ph. D. from the University of Toronto, both in chemistry. He is the author of papers on the chemistry of sulfur compounds, molecular rearrangements, and hydroprocessing.



---

# 1 Introduction

## 1.1 BASE STOCKS: GENERAL

Lubricants have been used by mankind from the very early days of civilization to assist in reducing the energy needed to slide one object against another. The first lubricants were animal fats, and much later whale oil was used. It was not until crude oil was discovered in commercial quantities in Oil Springs, Ontario, Canada, in 1858 and in Titusville, Pennsylvania, in the United States in 1859 that the concept of petroleum-based lubricants could be seriously considered on a large scale. The first petroleum refinery to produce base stocks (the petroleum distillates fractions used in lubricants) in the Western Hemisphere was built by Samuel Weir in Pittsburgh in the 1850s. One of the earliest lubricant producers (to reduce “waste” production) was the Standard Works in Cleveland, Ohio, owned in part by John D. Rockefeller, whose company subsequently became Standard Oil.

Other petroleum companies subsequently followed suit and the industry developed in size and scope over time as industrialization took hold and the demand for lubricants grew. Access to lubricants is essential to any modern society. Not only do lubricants reduce friction and wear by interposition of a thin liquid film between moving surfaces, they also remove heat, keep equipment clean, and prevent corrosion. Applications include gasoline and diesel engine oils, machinery lubrication, and turbine, refrigeration, and transformer oils and greases. In 2005 the world’s production of base stocks from petroleum totaled some 920,000 barrels per day<sup>1</sup> (bpd), with 25% of that (231,000 bpd) being in North America. Currently ExxonMobil, at 140,000 bpd, is the world’s largest producer of base stocks, followed by Royal Dutch/Shell Group (78,000 bpd). The world’s largest (40,300 bpd) lube plant is Motiva Enterprise’s Port Arthur plant;<sup>2</sup> Motiva is a 50/50 joint venture between Shell Oil and Saudi Refining. The annual world production volume is about equivalent to that of two to three large refineries, but lube production is dispersed across the world and annual production volume per plant is quite small (e.g., in North America, the average size is 10,000 bpd and in Europe it is 6600 bpd). Lube plants are usually part of fuel refineries.

The subject of this book is the chemistry of petroleum base stocks and of their manufacturing processes from crude oil fractions. Petroleum base stocks are hydrocarbon-based liquids, which are the major component (80% to 98% by volume) of finished lubricants, the remaining 2% to 20% being additives to improve performance. Therefore this book does not deal with the manufacture of nonpetroleum base stocks such as synthetics (from olefins such as 1-decene), ester-based ones, and others.

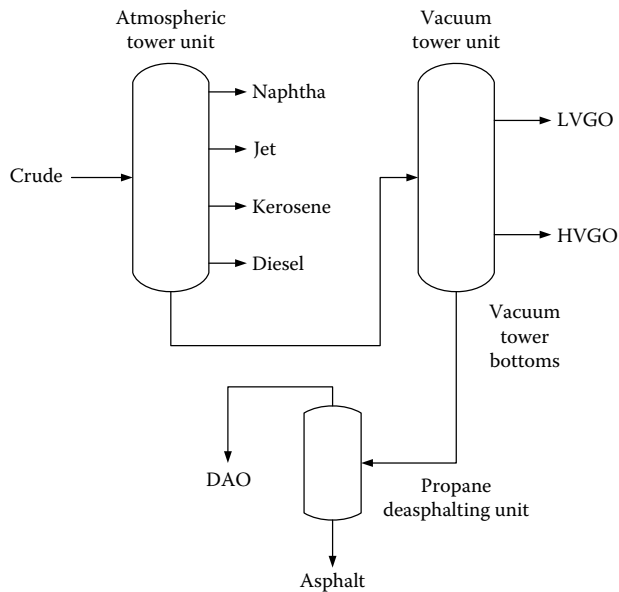
Base stocks usually have boiling ranges between 600°F and 1100°F at atmospheric pressure (some are lighter) and lube feedstocks therefore come from the

high-boiling region—the vacuum gas oil fraction and residue—of crude oil. Base stock boiling ranges may extend over several hundred degrees Fahrenheit. For the purpose of engine oil quality assurance, the American Petroleum Institute (API) has defined a base stock “as a lubricant component that is produced by a single manufacturer to the same specifications (independent of feed source or manufacturer’s location); that meets the same manufacturer’s specification; and that is identified by a unique formula, product identification number or both...”<sup>3</sup> A base oil is defined as “the base stock or blend of base stocks used in an API-licensed oil,” while a base stock slate is “a product line of base stocks that have different viscosities but are in the same base stock grouping and from the same manufacturer.” Alternatively the “slate” is the group of base stocks from a lube process that differ in viscosities, and there may be five or six from any given plant. Although they are referenced for other applications, API base stock applications apply mainly to components used in engine oils.

Base stocks are classified into two broad types—naphthenic and paraffinic—depending on the crude types they are derived from. Naphthenic crudes are characterized by the absence of wax or have very low levels of wax so they are largely cycloparaffinic and aromatic in composition; therefore naphthenic lube fractions are generally liquid at low temperatures without any dewaxing. On the other hand, paraffinic crudes contain wax, consisting largely of *n*- and iso-paraffins which have high melting points. Waxy paraffinic distillates have melting or pour points too high for winter use, therefore the paraffins have to be removed by dewaxing. After dewaxing, the paraffinic base stocks may still solidify, but at higher temperatures than do naphthenic ones because their molecular structures have a more paraffinic “character.” Paraffinic base stocks are preferred for most lubricant applications and constitute about 85% of the world supply.

## 1.2 BASE STOCKS FROM CRUDES

Within a naphthenic or paraffinic type, base stocks are distinguished by their viscosities and are produced to certain viscosity specifications. Since viscosity is approximately related to molecular weight, the first step in manufacturing is to separate out the lube precursor molecules that have the correct molecular weight range. This is done by distillation. Figure 1.1 provides a schematic of the hardware of a crude fractionation system in a refinery used to obtain feedstocks for a lube plant. Lower-boiling fuel products of such low viscosities and volatilities that they have no application in lubricants—naphtha, kerosene, jet, and diesel fuels—are distilled off in the atmospheric tower. The higher molecular weight components which do not vaporize at atmospheric pressure are then fractionated by distillation at reduced pressures of from 10 mmHg to 50 mmHg (i.e., vacuum fractionation). Thus the “bottoms” from the atmospheric tower are fed to the vacuum tower, where intermediate product streams with generic names such as light vacuum gas oil (LVGO) and heavy vacuum gas oil (HVGO) are produced. These may be either narrow cuts of specific viscosities destined for a solvent refining step or broader cuts destined for hydrocracking to lubes and fuels.



**FIGURE 1.1** Schematic of a refinery crude fractionation train and deasphalting unit.

The vacuum tower bottoms may contain valuable high-viscosity lube precursors (boiling point greater than 950°F) and these are separated from asphaltic components (these are black, highly aromatic components that are difficult to refine) in a deasphalting unit. Deasphalting units separate asphalt from refinable components by solubility, and this is usually solubility in propane for lube purposes. This waxy lube feedstock is called deasphalted oil (DAO). Further refining of the DAO—dewaxing and solvent refining or hydrotreatment—produces bright stock, which is a heavy (very viscous) base stock that is a “residue” (i.e., it is not a distillate overhead). The DAO can also be part of the feed to a lube hydrocracker to produce heavier base stocks. Representative boiling and carbon number ranges for feedstocks are given in Table 1.1—they will vary somewhat from refinery to refinery and depend on the needs of the specific lube processes employed and those of fuel production.

The waxy distillates and DAO require three further processing steps to obtain acceptable base stock:

- Oxidation resistance and performance must be improved by removal of aromatics, particularly polyaromatics, nitrogen, and some of the sulfur-containing compounds.
- The viscosity-temperature relationship of the base stock (improve the viscosity index [VI]) has to be enhanced—by aromatics removal—to meet industry requirements for paraffinic stocks.

**TABLE 1.1**  
**Representative Boiling and Carbon Number Ranges**  
**for Lube Feedstocks**

| Fraction | Approximate Boiling Point Range (°F) | Carbon Number Range <sup>a</sup> |
|----------|--------------------------------------|----------------------------------|
| LVGO     | 600–900                              | 18–34                            |
| HVGO     | 800–1100                             | 28–53                            |
| DAO      | 950+                                 | 38+                              |

<sup>a</sup> Carbon number ranges are referred to by the boiling points of the nearest n-paraffins; for example, the carbon number range of a 650–850°F fraction is C<sub>20</sub>–C<sub>30</sub> (651–843°F).

- The temperature at which the base stock “freezes” due to crystallization of wax must be lowered by wax removal so that equipment can operate at winter temperatures.

There are two strategic processing routes by which these objectives can be accomplished:

Processing steps which act by chemical separation: The undesirable chemical compounds (e.g., polyaromatics) are removed using solvent-based separation methods (solvent refining). The by-products (extracts) represent a yield loss in producing the base stock. The base stock properties are determined by molecules originally in the crude, since molecules in the final base stock are unchanged from those in the feed;

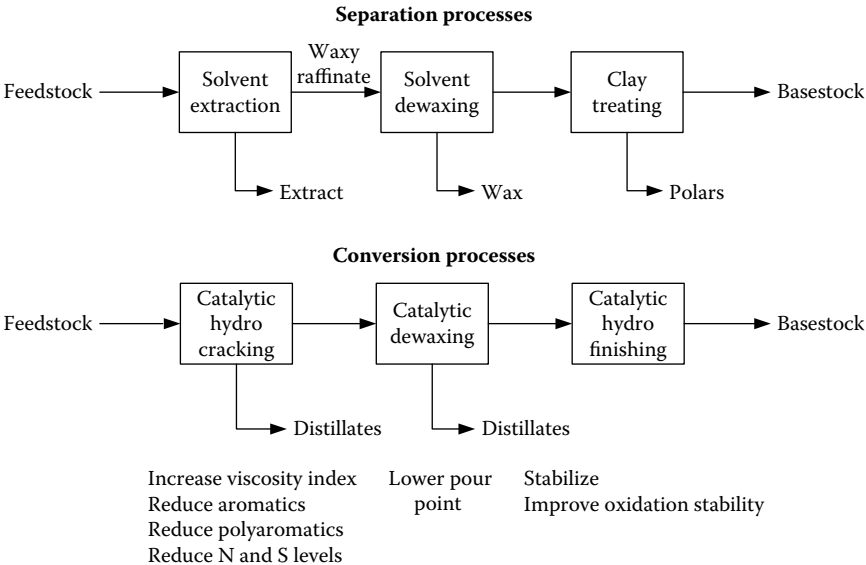
or

Processing steps which act by chemical conversion: Components with chemical structures unsuitable for lubes are wholly or partially converted to acceptable base stock components. These processes all involve catalysts acting in the presence of hydrogen, thus they are known collectively as catalytic hydroprocessing. Examples are the hydrogenation and ring opening of polyaromatics to polycyclic naphthenes with the same or fewer rings and the isomerization of wax components to more highly branched isomers with lower freezing points. Furthermore, the chemical properties of existing “good” components may be simultaneously altered such that even better performance can be achieved. Conversion processes are generally considered to offer lower operating costs, superior yields and higher base stock quality. In conversion processes, the eventual base stock properties reflect to some degree the molecules originally in the feed, but the extent of chemical alteration is such that products from different feedstocks can be very similar.

Separation processes are often depicted as “conventional” technologies and these solvent refining processes currently account for about 75% of the world’s

paraffinic base stock production. Conversion processes account for the remaining 25% and use catalytic hydroprocessing technology developed since World War II. This route has become particularly significant in North America, where more than 50% of base stock production uses this route. Some companies have chosen to combine separation and conversion, since the latter has been developed in steps and opportunities for synergism and the reuse of existing hardware have been recognized.

Figure 1.2 demonstrates how separation and conversion processes achieve the same end by different means. In the conventional solvent refining sequence, a polar solvent selectively extracts aromatics, particularly those with several aromatic rings and polar functional groups, resulting in an aromatic extract (the reject stream) and an upgraded waxy “raffinate” whose viscosity is less than that of the feed due to the removal of these polyaromatics. The major purposes of the extraction step are to reduce the temperature dependence of the viscosity (i.e., increase the VI) of the raffinate and improve the oxidation stability of the base stock. Since the raffinate still contains wax, which will cause it to “freeze” in winter, the next step—dewaxing—removes the wax. Again, a solvent-based method is used; in this case, crystallization of wax. This reduces the temperature at which the oil becomes solid—essentially the pour point. If desired, the wax can subsequently be de-oiled to make hard wax for direct commercial sale. The base stock now has almost all the desirable properties, however, in a last step it is usually subjected to clay treatment, which improves color and performance by



**FIGURE 1.2** Comparison of process schematics for separation and conversion process routes for lubes.



taking out a few percent largely composed of polyaromatics and nitrogen, sulfur, and any oxygen compounds. This clay treating step has now been largely replaced by a catalytic hydrofinishing step.

In the conversion process, catalytic hydrogenation in the first stage lube hydrocracking unit saturates part of the feedstock aromatics by hydrogenating them to cycloparaffins and also promotes significant molecular reorganization by carbon-carbon bond breaking to improve the rheological (flow) properties of the base stock (again improving the VI). Usually in this stage, feed sulfur and nitrogen are both essentially eliminated. Some of the carbon-carbon bond breaking produces overheads in the form of low-sulfur gasoline and distillates. The fractionated waxy lube streams, usually those boiling above about 700°F, are then dewaxed, either by solvent dewaxing or, more frequently, by catalytic hydroprocessing (in which either wax is cracked to gasoline or isomerized to low melting isoparaffins in high yields and which has a positive effect on VI). The final step in conversion processes is usually catalytic hydrogenation to saturate most of the remaining aromatics to make base stocks stable for storage and to improve their performance. Base stocks produced by this route are frequently water white, whereas solvent extracted stocks retain some color. The advantages of the conversion route are many: less dependence on supplies of expensive high-quality “lube” crudes, which the solvent refining process requires and which are increasingly in short supply, higher base stock yields, and lubricants that better (and in some cases exclusively) meet today’s automotive lubricant requirements.

### 1.3 BASE STOCK PROPERTIES

Base stocks are manufactured to specifications that place limitations on their physical and chemical properties, and these in turn establish parameters for refinery operations. Base stocks from different refineries will generally not be identical, although they may have some properties (e.g., viscosity at a particular temperature) in common. At this point it is worth briefly reviewing what measurements are involved in these specifications, what they mean, and where in the process they are controlled.

Starting with density, the most important ones that describe physical properties are

- Density and gravity, °API: Knowledge of the density is essential when handling quantities of the stock and the values can also be seen to fit with the base stock types. An alternative measure is the API gravity scale where

$$\text{API gravity} = 141.5/\text{specific gravity} - 131.5.$$

- Density increases with viscosity, boiling range, and aromatic and naphthenic content, and decreases as isoparaffin levels increase and as VI increases.

- Viscosity measured at 40°C and 100°C: Base stocks are primarily manufactured and sold according to their viscosities at either 40°C or 100°C, using kinematic viscosities (see later). Viscosity “grades” are now defined by kinematic viscosity in centistokes (cSt) at 40°C; formerly they were established on the Saybolt universal seconds (SUS) scale at 100°F. Higher viscosity base stocks are produced from heavier feedstocks (e.g., a 100 cSt at 40°C oil is produced from a HVGO and cannot be made from a LVGO since the molecular precursors are not present). As viscosity increases, so does the distillation midpoint.
- Viscosity index (VI): VI is a measure of the extent of viscosity change with temperature; the higher the VI, the less the change, and generally speaking, higher VIs are preferred. VI is usually calculated from measurements at 40°C and 100°C. The minimum VI for a paraffinic base stock is 80, but in practice the norm is 95, established by automotive market needs. Naphthenic base stocks may have VIs around zero. The conventional solvent extraction/solvent dewaxing route produces base stocks with VIs of about 95. Lower raffinate yields (higher extract yields) in solvent refining mean higher VIs, but it is difficult economically to go much above 105. In contrast, conversion processes enable a wide VI range of 95 to 140 to be attained, with the final product VI depending on feedstock VI, first stage reactor severity, and the dewaxing process. Dewaxing by hydroisomerization gives the same or higher VI relative to solvent dewaxing. To obtain a VI greater than 140, the feedstock generally must be either petroleum wax or Fischer-Tropsch wax.
- Pour point: The pour point measures the temperature at which a base stock no longer flows, and for paraffinic base stocks, pour points are usually between −12°C and −15°C, and are determined by operation of the dewaxing unit. For specialty purposes, pour points can be much lower. The pour points of naphthenic base stocks, which can have very low wax content, may be much lower (−30°C to −50°C). For very viscous base stocks such as Bright stocks, pour points may actually reflect a viscosity limit. Pour points are measured traditionally by ASTM D97,<sup>4</sup> but three new automated equivalent test methods are the “tilt” method (ASTM D5950), the pulse method (ASTM D5949), and the rotational method (ASTM D5985).
- Cloud point: The cloud point is the temperature at which wax crystals first form as a cloud of microcrystals. It is therefore higher than the pour point, at which crystals are so numerous that flow is prevented. The longstanding ASTM method is D2500, with three new automated methods being ASTM D5771, D5772, and D5773. Many base stock inspection sheets no longer provide cloud points. Cloud points can be 3°C to 15°C above the corresponding pour points.
- Color: Solvent extracted/solvent dewaxed stocks will retain some color as measured by ASTM D1500. Hydrocracked stocks, when hydrofinished at high pressures, are usually water white and their color is best measured on the Saybolt color scale (ASTM D156).

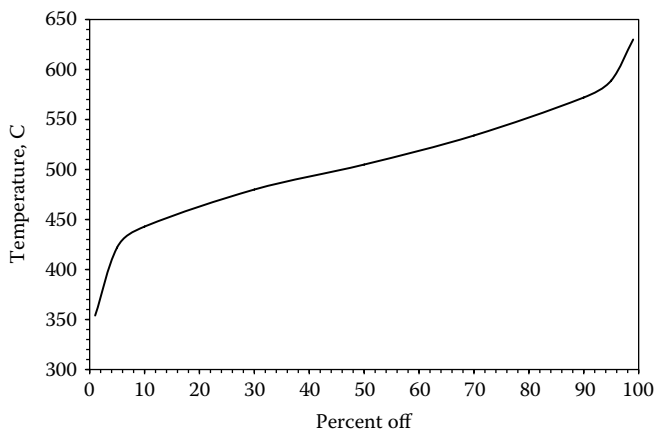
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**TABLE 1.2**  
**SimDist of a 500N Base Stock**

| Percent Off | Temperature (°C) |
|-------------|------------------|
| 1           | 354              |
| 5           | 422              |
| 10          | 443              |
| 30          | 480              |
| 50          | 505              |
| 70          | 534              |
| 90          | 572              |
| 95          | 589              |
| 99          | 630              |

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- Distillation: At one time this would have been carried out using an actual physical distillation using either ASTM D86, a method performed at atmospheric pressure and applicable to very light lubes, or by vacuum distillation according to ASTM D1160 for heavier ones. Neither of these methods is employed much for base stocks nowadays because of their time and manpower requirements. Distillation today is usually performed by gas chromatography and the method is commonly called either simulated distillation (SimDist) or gas chromatographic distillation (GCD) using ASTM D2887. This method is capable of excellent accuracy, repeatability, and fast turnaround times and is normally automated. It is applicable to samples with final boiling points of less than 1000°F (538°C). For very heavy samples, ASTM WK2841 can analyze samples with boiling points in the range of 345°F to 1292°F (174°C to 700°C) (C10–C90). Results are usually reported as a table (e.g., Table 1.2) or graphically (as in Figure 1.3) in either degrees Fahrenheit or Celsius.
- Appearance: Base stocks should be “clear and bright” with no sediment or haze.
- Flash point: The flash point measures the temperature at which there is sufficient vapor above a liquid sample to ignite and is a significant feature in product applications where it is used as a common safety specification. Flash points are a reflection of the boiling point of the material at the front end of the base stock’s distillation curve. Flash points generally increase with viscosity grade. High flash points for a given viscosity are desirable. Good fractionation and increased base stock VIs favor higher flash points. The Cleveland Open Cup method (ASTM D92) is the most often cited for North American base stocks, while the Pensky-Martens test (ASTM D93) is sometimes used.
- Volatility: This has emerged as a significant factor in automotive lubricant products from environmental and operational standpoints and again pertains predominantly to the distillation front end. Low volatility



**FIGURE 1.3** SimDist (or GCD) representation of a base stock's distillation profile.

(minimal losses at high temperatures) reduces emissions, is beneficial for emissions catalysts, reduces oil consumption, and helps prevent engine oil viscosity changes. Volatility is obviously affected by viscosity grade, but for a constant viscosity is established in part by sharper fractionation and in part by VI. It is measured either by the Noack method (ASTM D5800), using a thermogravimetric (TGA) method (namely ASTM D6375), or by gas chromatography (ASTM D6417 for engine oils).

- Aniline point: This is a measure of the ability of the base stock to act as a solvent and is determined from the temperature at which equal volumes of aniline and the base stock are soluble (ASTM D611). High aniline points (approximately 100°C or greater) imply a paraffinic base stock, while low aniline points (less than 100°C) imply a naphthenic or aromatic stock.
- Viscosity gravity constant: This is an indicator of base stock composition and solvency that is calculated from the density and viscosity according to ASTM D2501; it usually has a value between 0.8 and 1.0. High values indicate higher solvency and therefore greater naphthenic or aromatic content. This is usually of interest for naphthenic stocks. See Chapter 4 for further details.
- Refractive index: The refractive index is used to characterize base stocks, with aromatic ones having higher values than paraffinic ones. The value increases with molecular weight.
- Refractivity intercept: This is calculated (ASTM D2159) from the density ( $d$ ) and refractive index ( $n$ ) (both at 20°C) using the sodium D line (ASTM D1218), where

$$\text{Refractivity intercept} = n - (d/2),$$

and is a means of characterizing the composition of the sample. Values range from 1.03 to 1.047.

- Brookfield low temperature viscosity (ASTM D2983): This is the low temperature shear rate apparent viscosity measurement between  $-5^{\circ}\text{C}$  and  $-40^{\circ}\text{C}$  and is reported in centipoise (cP).
- Cold cranking simulator: The apparent low temperature viscosity of engine oils (ASTM D5293) correlates with the ease of low temperature engine cranking, measured in centipoise rather than centistokes, and the temperature is always given (e.g., CCS at  $-25^{\circ}\text{C}$  = 1405 cP).

Chemical and compositional property measurements include the following:

- Sulfur: Sulfur is present in all lube plant feedstocks fractionated from crude oil and its content may be up to several percentage points. Solvent refining removes some but not all, therefore such stocks with no further treatment can contain up to several mass percent of sulfur. Hydrofinishing of solvent refined stocks can reduce this level substantially. Base stocks from conversion processes will have sulfur levels in the low parts per million (ppm) range since sulfur is relatively easily removed in severe hydroprocessing.
- Nitrogen: Like sulfur, nitrogen is present in all lube feedstocks, generally in the 500 to 2000 ppm range. These levels are reduced by solvent extraction and nearly eliminated by hydrocracking.
- Aromatics: These are predominantly monoaromatics in both feedstocks and products, but substantial levels of di- and triaromatics can be present in feedstocks. Aromatics, particularly polyaromatics, worsen base stock oxidation stability and can be virtually eliminated by conversion processes. Solvent extracted stocks still contain substantial levels of aromatics. These can be measured by several methods, including supercritical fluid chromatography (ASTM D5186), high-pressure liquid chromatography (HPLC) (ASTM D6379), chromatography over alumina/silica gel (ASTM D2549), preparative chromatography (ASTM D2007), and ultraviolet (UV) spectroscopy.
- $\%C_A$ ,  $\%C_N$ ,  $\%C_P$ : These are the average carbon-type distributions, namely aromatic, naphthenic, and paraffinic. Aromatic carbons ( $C_A$ ) are those in aromatic rings. To give a simple example, toluene has six aromatic carbons and one paraffinic carbon, and for this the  $\%C_A$  is 86 and the  $\%C_P$  is 14. Tetralin has six aromatic carbons and four naphthenic ones. For hydrocracked base stocks, we would expect the  $\%C_A$  to be near zero. These parameters can be determined via the n-d-M method (ASTM D3238) and from viscosity-gravity constant and refractivity intercepts via ASTM D2140.  $\%C_A$  can also be determined by nuclear magnetic resonance (NMR) spectroscopy (ASTM D5292). The result will depend on the method employed. See Chapter 4 for more discussion of these compositional methods.

Table 1.3 provides inspection results for a range of base stocks of different origins. Since the values are representative of those types, some commentary is worthwhile. First, the general format of these tables is to list the inspections (tests) performed in the left-hand column, with the column to the right of that identifying

**TABLE 1.3**  
**Inspection Results for Hydrotreated Naphthenic, Solvent Refined,**  
**and Hydrocracked Base Stocks**

| Test                         | Source:         | A          | B          | C               | D            | E            |
|------------------------------|-----------------|------------|------------|-----------------|--------------|--------------|
|                              | Type:<br>Method | Naphthenic | Naphthenic | Solvent Refined | Hydrocracked | Hydrocracked |
| API gravity,<br>°API         | ASTM<br>D1298   | 29.8       | 24.0       | 29.0            | 32.0         | 38.1         |
| Density at<br>15°C, kg/L     | ASTM<br>D4052   | 0.877      | 0.910      | 0.8816          | 0.865        | 0.8343       |
| Viscosity, cSt<br>at 40°C    | ASTM<br>D445    | 7.5        | 29.8       | 30.0            | 42.0         | 39.5         |
| Viscosity, cSt<br>at 100°C   | ASTM<br>D445    | 2.07       | 4.55       | 5.09            | 6.3          | 6.7          |
| VI                           | ASTM<br>D2270   | 56         | 35         | 95              | 95           | 125          |
| Pour point,<br>°C            | ASTM<br>D97     | −54        | −39        | −15             | −15          | −18          |
| Sulfur, mass<br>%            | ASTM<br>D5185   | 0.03       | 0.09       | 0.45            | 15 ppm       | 6 ppm        |
| Nitrogen,<br>ppm             | ASTM<br>D5762   |            |            | 50              | <1           | <1           |
| Aniline point,<br>°C         | ASTM<br>D611    |            | 75         |                 |              |              |
| Color                        | ASTM<br>D1500   | L 0.5      | L 1.5      | L 0.5           | L 0.5        | L 0.5        |
| Appearance                   | ASTM<br>D4176   | C&B        |            |                 |              |              |
| Flash point,<br>°C           | ASTM<br>D92     | 151        | 157        | —               | —            | —            |
| Volatility,<br>Noack         | ASTM<br>D5800   | —          | —          | 20              | 13           | 5            |
| Aromatics, %                 | ASTM<br>D2007   | —          | —          | 20.5            | <1           | <1           |
| Hydrocarbon<br>type analysis | ASTM<br>D2140   |            |            |                 |              |              |
| C <sub>A</sub> , %           |                 | 4          |            |                 |              |              |
| Hydrocarbon<br>type analysis | ASTM<br>D3238   |            |            |                 |              |              |
| C <sub>A</sub> , %           |                 | 6          | —          | —               | —            | —            |
| C <sub>N</sub> , %           |                 | 52         | —          | —               | —            | —            |
| C <sub>P</sub> , %           |                 | 42         | —          | —               | —            | —            |

the test methods used. Identification of the source of the methods used contributes significantly towards “certifying” the numbers contained in the table. This same format is usually used for feedstocks and any intermediate products.

Within the table, the two naphthenic oils on the left-hand side have high densities relative to all the others, regardless of viscosity, because they are largely composed of cycloparaffins and aromatics. These naphthenic oils have the lowest pour points of the lot, reflecting the absence of paraffinic structures, the feature they are best known for. In contrast, base stock E has the lowest density of this group because it is highly paraffinic (high VI) and paraffins and paraffin-like molecules are low density components. Base stocks D and E have extremely low sulfur levels because they have been severely hydrotreated. In contrast, the solvent extracted C has a sulfur content of 0.25%, which alone labels it as a solvent extracted oil, but more severe hydrofinishing could have reduced the levels much further. The very high VI of E shows that this cannot be a solvent extracted stock since that process route cannot economically achieve such high VIs. Finally, for D, produced by lube hydrocracking followed by dewaxing using isomerization, its very low sulfur, nitrogen, and aromatics contents are outcomes of these routes.

## 1.4 FEEDSTOCKS AND BASE STOCKS: GENERAL COMPOSITIONAL ASPECTS

Petroleum distillates and residues contain a complexity of hydrocarbons, some of which have already been mentioned, together with sulfur and nitrogen compounds. These were originally complex enough, being of plant origin, but after spending several million years buried at high temperatures, identification of individual structures is only possible for those with the lowest molecular weight (i.e., in the case of some naphtha components, where the number of isomers is limited). Table 1.4 illustrates the complexity using the simplest of hydrocarbon classes, the n-paraffins.<sup>5</sup>

As a consequence, we have to rely on the identification of groups or “lumps” of compounds that fall into similar chemical classifications. This approach has been quite successful as a means of either separating or quantifying them by instrumental methods.

Beginning with the simplest, these chemical groups are (Figure 1.4)

- n-Paraffins: These are C<sub>18</sub> and greater members of the n-paraffin homologous series, which are present in significant quantities in feeds and waxy intermediate streams with a boiling range of 600°F to 850°F, depending on the wax content of the feed. As the boiling point increases beyond 850°F, they become much less common. n-Paraffins are easily identified and quantified by gas chromatography because they give sharp peaks and can be concentrated in the slack wax fraction from solvent dewaxing. They are significant because they have high melting points and therefore increase the pour point of base stocks. Base stocks with low n-paraffin contents have low pour points (e.g., naphthenics).

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**TABLE 1.4**  
**Carbon Number of n-Paraffins**  
**and the Number of Isomers**

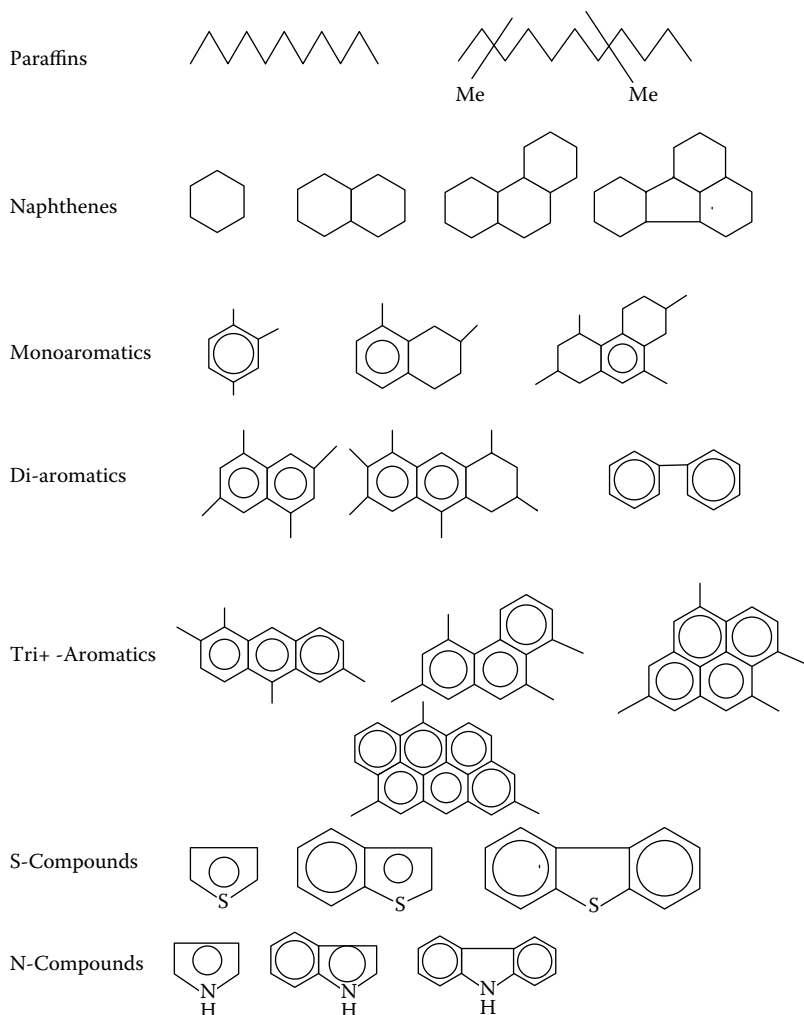
| Carbon Number | Isomers               |
|---------------|-----------------------|
| 5             | 3                     |
| 8             | 18                    |
| 10            | 75                    |
| 12            | 355                   |
| 15            | 4347                  |
| 20            | $3.66 \times 10^5$    |
| 25            | $3.67 \times 10^7$    |
| 30            | $4.11 \times 10^9$    |
| 35            | $4.93 \times 10^{11}$ |
| 40            | $6.24 \times 10^{13}$ |

*Source:* K.H. Altgelt and M.M. Boduzyński, Composition and Analysis of Heavy Petroleum Fractions (New York: Marcel Dekker 1993) With permission.

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- Isoparaffins: These have n-paraffin backbones with alkyl branches; on an isoparaffin chain there may well be several branches of methyl groups or higher. Those isoparaffins most similar in structure to n-paraffins (e.g., single branches near a chain end) have higher pour points and will be removed by solvent dewaxing. Identification of individual members may be quite difficult. Isoparaffins as a group are commonly said to have high VIs and low pour points, and confer good oxidation resistance. They are therefore a sought-after component in base stocks. Polyalphaolefins (PAOs) are synthetic isoparaffinic base stocks that are of high commercial value because of their low pour points and excellent performance; they are not discussed in this book.
- Cycloparaffins (naphthenes): Cycloparaffins contain one or more cyclohexane or cyclopentane rings, or a combination thereof. If several rings are present, these are usually in the condensed form, presumably because of their natural origin. Mass spectroscopy of the saturates fraction can identify the number of rings and the percentage of the molecules having each number of rings. Alkyl substituents on the rings are branched and unbranched alkyl groups. Monocycloparaffins with 1,4 substituents are widely regarded as favorable structures, whereas polynaphthenes (3 + rings) are considered unfavorable for both VI and oxidation resistance.
- Aromatics: Basic structures have one to six or more benzene rings with some of the carbon–hydrogen bonds replaced by carbon–carbon bonds of alkyl substituents. Generally frequency declines with an increasing number of rings. Alkyl-substituted benzenes with 1,4 alkyl groups have





**FIGURE 1.4** Basic chemical types present in lube feedstocks and in many base stocks.

high VIs and good oxidation resistance, whereas fused polyaromatic structures are undesirable.

- **Sulfur-containing compounds:** These may be thiols, sulfides, thiophenes, benzo- and dibenzo-thiophenes, and more complex structures. Solvent extraction reduces measured sulfur levels and therefore the content of sulfur compounds in solvent refined lubes; in solvent refined lubes, oxidation studies show that there appears to be an optimum level for sulfur compounds. Lube hydrocracking generally will reduce sulfur to about 10 ppm or less in the base stocks. The 4,6-di-alkyl

substituted dibenzothiophenes are the most resistant type of sulfur compounds to hydrotreating (due to steric hindrance), while thiols and sulfides are the most easily hydrogenated. Sulfur compounds constitute a poison to hydroisomerization dewaxing catalysts and to nickel and noble metal catalysts and must be reduced to low levels in the feeds to those catalyst types.

- Nitrogen-containing compounds: Nitrogen largely appears in pyrroles, benzo- and dibenzo-carbazoles, pyridines, and quinolines. Nitrogen compounds are best minimized in finished lubes since they contribute to color formation. Lube hydrocracking reduces nitrogen levels to a few parts per million.
- Oxygen-containing compounds: Compounds containing chemically bound oxygen (e.g., furans, carboxylic acids, etc.) in lube feedstocks are seldom an issue and as a rule are overlooked.

1.5 API BASE STOCK CLASSIFICATIONS

A framework in which base stocks are differentiated from one another for the purpose of base stock interchanges came with the development of base stock categories by the API in 1993 (Table 1.5).<sup>6</sup> There are now five categories, three of which apply to paraffinic stocks and one to naphthenics. Paraffinic base stocks fall into categories I–III, and there are just three criteria involved—sulfur content, the percentage of saturates, and the VI—in determining the category of a particular stock. It should be noted that groups II+ and III+ are not official categories. These terms are employed in marketing, but are frequently referred to, hence their inclusion in Table 1.5.

The criteria for group I stocks places no limitations on sulfur content or percent aromatics, and in practice these are essentially all solvent refined. To reduce the aromatics content to less than 10% generally requires catalytic hydro-processing equipment. The VI range here is broad (80 to 120) and in practice

TABLE 1.5  
API Paraffinic Base Stock Categories

| Group | Sulfur, Mass %   |        | Saturates, Mass % |  | VI           |
|-------|--|--------|-------------------|--|--------------|
| I     | >0.03  | and/or | <90               |  | ≥80 to <120  |
| II    | ≤0.03  | and    | ≥90               |  | ≥80 to <120  |
| II+   | ≤0.03  | and    | ≥90               |  | ≥110 to <119 |
| III   | ≤0.03  | and    | ≥90               |  | ≥120         |
| III+  | ≤0.03  | and    | >90               |  | ≥130<150     |
| IV    | All polyalphaolefins [PAOs]                                      |        |                   |  |              |
| V     | All stocks not included in groups I–IV (e.g., esters, pale oils) |        |                   |  |              |

Source: The American Petroleum Institute, Publication 1509. With permission.

most solvent refined base stocks produced have VIs of 95 to 105. Generally a VI of 95 is about the market minimum. High VIs are expensive to obtain by solvent extraction since yields decline rapidly as VI rises.

Base stocks falling in the group II category will, in the vast majority of cases, be hydrocracked stocks, since the low sulfur and high saturates limits (low aromatics of less than 10%) are otherwise difficult to attain. The majority of group II stocks produced have VIs of 95 to 105. Group II+ is a commonly used industry subset (not a formal part of the API classification) defined by a VI in the range of 110 to 120 and created because of the current demand for the low volatility that accompanies these VIs.

Group III base stocks are differentiated by their very high VIs, which defines them as being products from either fuel hydrocracking units (which operate at high severities and low lube yields) or by hydrocracking or isomerizing wax. Group III+, like group II+, is an informal subset. Group III+ base stocks are sourced mainly from gas-to-liquids (GTL) plants.

Group IV base stocks are polyalphaolefins and originate from long-chain terminal olefins (e.g., 1-decene). Group V includes any base stocks not defined by groups I–IV, such as naphthenic base oils, esters, polyglycols, and polyinternalolefins.

## 1.6 VISCOSITY GRADES FOR INDUSTRIAL LUBRICANTS

Each refinery usually produces a limited number (5 to 12) of base stocks, since each base stock requires that there be economically sufficient precursors in the front-end feed and, as well, in the feed to the final fractionation after all processing is complete. In addition, the refinery tries to adjust production rates for individual base stocks to meet their demand. Today, base stocks are classified by their viscosity in square millimeters per second ( $\text{mm}^2/\text{s}$ ) (or centistokes) measured at 40°C and usually employ the International Organization for Standardization (ISO) system for industrial lubricants (ASTM D2422), with a range of 2 to 3200 cSt. Twenty viscosity grades and their ranges are provided in Table 1.6.<sup>7</sup>

Previously it had been customary to assign viscosity grades according to SUS viscosities at 100°F. The SUS grades corresponding to the ISO grades are given in the right-hand column of Table 1.6. SUS viscosities are rarely directly measured any longer—where there is a need for those numbers, they are calculated from kinematic viscosities at 40°C and 100°C. However, SUS names and grades have had remarkable staying power and are still employed in the naming systems employed by various companies (e.g., an ISO 22 is frequently [usually in North America] called a 100N and an ISO 100 is called a 500N). This is done to avoid customer confusion in changing names. To add to the confusion, some companies, particularly with regard to base stocks for automotive applications, designate their products by viscosity at 100°C and therefore these are called 4 cSt (ISO 22) or 10 cSt (ISO 100) products. For an informative article on viscosity grades see “ISO Viscosity Grades” by M. Johnson.<sup>8</sup>

**TABLE 1.6**  
**ISO Viscosity System for Industrial Fluid Lubricants**

| Grade<br>Identification | Midpoint,<br>cSt at 40°C | Viscosity Limits,<br>cSt at 40°C | American SUS<br>Grades (Range) |
|-------------------------|--------------------------|----------------------------------|--------------------------------|
|                         |                          | Minimum–Maximum                  |                                |
| ISO VG 2                | 2.2                      | 1.98–2.4                         | 32 (32.0–34.0)                 |
| ISO VG 3                | 3.2                      | 2.88–3.44                        | 36 (35.5–37.5)                 |
| ISO VG 5                | 4.6                      | 4.14–5.06                        | 40 (39.5–42.5)                 |
| ISO VG 7                | 6.8                      | 6.12–7.48                        | 50 (46.0–50.5)                 |
| ISO VG 10               | 10                       | 9.00–11.0                        | 60 (55.5–62.5)                 |
| ISO VG 15               | 15                       | 13.5–16.5                        | 75 (71.5–83.5)                 |
| ISO VG 22               | 22                       | 19.8–24.2                        | 105 (97.0–116)                 |
| ISO VG 32               | 32                       | 28.8–35.2                        | 150 (136–165)                  |
| ISO VG 46               | 46                       | 41.4–50.6                        | 215 (193–235)                  |
| ISO VG 68               | 68                       | 61.2–74.8                        | 315 (284–347)                  |
| ISO VG 100              | 100                      | 90.0–110                         | 465 (417–510)                  |
| ISO VG 150              | 150                      | 135–165                          | 700 (625–764)                  |
| ISO VG 220              | 220                      | 198–242                          | 1000 (917–1121)                |
| ISO VG 320              | 320                      | 288–352                          | 1500 (1334–1631)               |
| ISO VG 460              | 460                      | 414–506                          | 2150 (1918–2344)               |
| ISO VG 680              | 680                      | 612–748                          | 3150 (2835–3465)               |
| ISO VG 1000             | 1000                     | 900–1100                         | 4650 (4169–5095)               |
| ISO VG 1500             | 1500                     | 1350–1650                        | 7000 (4169–5095)               |
| ISO VG 2200             | 2200                     | 1980–2420                        | 10,200 (9180–11,221)           |
| ISO VG 3200             | 3200                     | 2880–3520                        | 14,840 (13,355–16,324)         |

*Source:* ASTM, ASTM D2422. With permission.

**1.7 SOCIETY FOR AUTOMOTIVE ENGINEERS**  
**VISCOSITY CLASSIFICATION FOR ENGINE OILS**

The Society for Automotive Engineers (SAE) has developed a viscosity classification system for finished (i.e., not just the base stock) engine lubricants that defines viscosity ranges as well as low temperature properties. The 2004 SAE J300 grades are shown in Table 1.7.<sup>9</sup>

Single-grade winter oils, 0W through 25W, specify minimum hot viscosities (at 100°C) and maximum viscosities at low temperatures to ensure easy starting. SAE grades 20 through 60 are not intended for winter use. Multigrade oils define low and high temperature properties to provide additional engine protection (e.g., a 5W30 oil meets the low temperature requirements of a 5W oil and its viscosity at high temperature falls within the viscosity range for a 30 grade oil; that is,

**TABLE 1.7**  
**SAE Viscosity Grades for Engine Oils, J300 (2004)**

| SAE Viscosity Grade | Viscosity (cP) at Temperature (°C), Maximum |                 | Viscosity, mm <sup>2</sup> /sec (cSt) at 100°C |         |
|---------------------|---|-----------------|--|---------|
|                     | Cranking                                    | Pumpability     | Minimum  | Maximum |
| 0W                  | 6200 at -35°C                               | 60,000 at -40°C | 3.8  | —       |
| 5W                  | 6600 at -30°C                               | 60,000 at -35°C | 3.8  | —       |
| 10W                 | 7000 at -25°C                               | 60,000 at -30°C | 4.1  | —       |
| 15W                 | 7000 at -20°C                               | 60,000 at -25°C | 5.6  | —       |
| 20W                 | 9500 at -15°C                               | 60,000 at -20°C | 5.6  | —       |
| 25W                 | 13,000 at -10°C                             | 60,000 at -15°C | 9.3  | —       |
| 20                  | —   | —               | 5.6  | <9.3    |
| 30                  | —   | —               | 9.3  | <12.5   |
| 40                  | —   | —               | 12.5   | <16.3   |
| 50                  | —   | —               | 16.3   | <21.9   |
| 60                  | —   | —               | 21.9   | <26.1   |

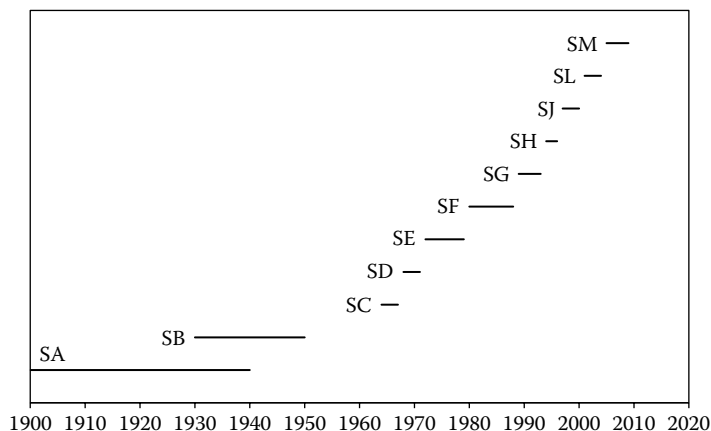
Source: Society of Automotive Engineers/SAE J300. With permission.

overall the viscosity of the oil changes less with temperature than that of a single-grade winter oil).

## 1.8 API ENGINE OIL CLASSIFICATIONS

As both gasoline and diesel engine technology advances, new demands are placed on lubricant performance and it becomes important to clearly distinguish the appropriate applications of engine lubricants from different manufacturers. Thus, in the United States, the API together with the SAE and ASTM identify lubricant standards at intervals as engine technology needs require. This classifies engine oils according to their performance and related to their intended type of service. In Japan, the lubricant specification organization is the Japanese Automotive Standards Organization (JASO), while in Europe it is the Association des Constructeurs Européens d'Automobiles (ACEA). A further significant body is the International Lubricant Specification and Approval Committee (ILSAC), which is a body composed of U.S. and Japanese engine manufacturers (General Motors, Ford, DaimlerChrysler, Toyota, and Honda) whose specifications apply mainly to North America and Japan.

Both gasoline and diesel engine classifications are letter grades, preceded by "S" (service) for gasoline engine lubricants and by "C" (commercial) for diesel engine lubricants. Gasoline engine oil classifications and the time periods they have been in force are shown in Figure 1.5. ILSAC gasoline engine certifications are indicated by GF-X, where X is a number. So far these have corresponded to API certifications, namely GF-1 = SH, GF-2 = SJ, GF-3 = SL, and GF-4 = SM.



**FIGURE 1.5** API gasoline engine oil classifications since 1900.

The significance of these classifications to base stock manufacturers is that they influence the selection of base stock types (API groups I–V) and the properties that are employed to blend engine oils. Since about 60% of worldwide lubricant demand<sup>10</sup> is for engine oils, the classifications tend to drive new manufacturing technology for all paraffinic base stocks. And of course the reverse occurs, as base stocks are produced by new technologies, engine lubricant developers use these to develop more advanced engine designs, which then provides drivers for new manufacturing technology. Figure 1.5 shows that in the 1900 to 1960 period, engine oil development was very slow, but since then the pace has picked up noticeably such that engine, environmental, and marketplace developments have required new categories every three to four years.

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