11.1. INTRODUCTION

In the present context, the term mineral oil or white oil refers to colorless or very pale oils within the lubricating oil class as regards carbon number and boiling range (Table 11.1, Fig. 11.1). Minerals (mineral) oils belong to two main groups, medicinal (pharmaceutical) oils and technical oils, the chief difference being degree of refining (Gruse and Stevens, 1960; Guthrie, 1967; Biske, 1973; Weissermel and Arpe, 1978; Francis and Peters, 1980; Hoffman, 1983; Austin, 1984; Chenier, 1992; Hoffman and McKetta, 1993; Warne, 1998; Speight, 2000; Banaszewski and Blythe, 2000).

Medicinal oils represent the most refined of the bulk petroleum products, especially when the principal use is for the pharmaceutical industry. Thus mineral oil destined for pharmaceutical purposes must meet stringent specifications to ensure that the oil is inert and that it does not contain any materials that are suspected to be toxic. Technical mineral oil (as opposed to pharmaceutical mineral oil) must meet much less stringent specifications requirements because the use is generally for transformer oil, cosmetic preparations (such as hair cream), in the plastics industry, and in textiles processing. Many of the same test methods are applied to all mineral oils, although the specifications will differ and oils for different uses will have to meet different standards of purity.

Technical oils find uses in different industries but in particular the electrical industry, where there is frequent use of transformer oil. Transformer oil can be divided into two main groups: (a) oils for transformers and switch gear and (b) oils for power cables; this latter group can be further subdivided into thin oils, for use in oil-filled (hollow core) cables, and more viscous oils, sometimes used as such in cable insulation but more commonly as components of cable impregnation compounds.

11.2. PRODUCTION AND PROPERTIES

Mineral oils are produced from selected petroleum fractions that are distilled to provide finished products with the desired viscosity. In addition to
Typically, mineral oil is distilled to specification from the required crude oil fraction followed by pretreatment by solvent extraction, hydrotreating, and dewaxing (Gruse and Stevens, 1967; Speight, 2000 and references cited therein). Application of hydrotreating (Speight, 2000) means that mineral oil can be produced without acid treatment. However, on occasion, there is still the need to exhaustively treat the selected feedstock with concentrated sulfuric acid (gaseous sulfur trioxide treatment also may be used) to remove the aromatic, unsaturated hydrocarbons and other impurities. Petroleum sulfonic acids, produced as by-products during acid treatment, are removed by extraction and neutralization. The oil can be refined even further to an ultimate degree of purity by adsorption.

The fraction chosen for refining may have been subjected to a preliminary refining with a differential solvent. The exact procedure for the acid treatment varies (Speight, 2000), but a preliminary acid treatment (chiefly for drying) may be followed by incremental addition of as much as 50% by volume of acid as strong as 20% fuming sulfuric acid. The sludge is promptly removed to limit oxidation-reduction reactions; the time, temperature, and method of application depend on the type of charge stock and the desired degree of refining. The product is neutralized with alkali and washed with ethyl or isopropyl alcohol or acetone to remove the oil-soluble sulfonic mahogany acids; water-soluble green

Table 11.1. General Summary of Product Types and Distillation Range

<table>
<thead>
<tr>
<th>Product</th>
<th>Lower Carbon Limit</th>
<th>Upper Carbon Limit</th>
<th>Lower Boiling Point °C</th>
<th>Upper Boiling Point °C</th>
<th>Lower Boiling Point °F</th>
<th>Upper Boiling Point °F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refinery gas</td>
<td>C₁</td>
<td>C₄</td>
<td>-161</td>
<td>-1</td>
<td>-259</td>
<td>31</td>
</tr>
<tr>
<td>Liquefied petroleum gas</td>
<td>C₃</td>
<td>C₄</td>
<td>-42</td>
<td>-1</td>
<td>-44</td>
<td>31</td>
</tr>
<tr>
<td>Naphtha</td>
<td>C₅</td>
<td>C₁₇</td>
<td>36</td>
<td>302</td>
<td>97</td>
<td>575</td>
</tr>
<tr>
<td>Gasoline</td>
<td>C₄</td>
<td>C₁₂</td>
<td>-1</td>
<td>216</td>
<td>31</td>
<td>421</td>
</tr>
<tr>
<td>Kerosene/diesel fuel</td>
<td>C₈</td>
<td>C₁₈</td>
<td>126</td>
<td>258</td>
<td>302</td>
<td>575</td>
</tr>
<tr>
<td>Aviation turbine fuel</td>
<td>C₈</td>
<td>C₁₆</td>
<td>126</td>
<td>287</td>
<td>302</td>
<td>548</td>
</tr>
<tr>
<td>Fuel oil</td>
<td>C₁₂</td>
<td>&gt;C₂₀</td>
<td>216</td>
<td>421</td>
<td>&gt;343</td>
<td>&gt;649</td>
</tr>
<tr>
<td>Lubricating oil</td>
<td>&gt;C₂₀</td>
<td>&gt;343</td>
<td>&gt;649</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wax</td>
<td>C₁₇</td>
<td>&gt;C₂₀</td>
<td>302</td>
<td>&gt;343</td>
<td>575</td>
<td>&gt;649</td>
</tr>
<tr>
<td>Asphalt</td>
<td>&gt;C₂₀</td>
<td>&gt;343</td>
<td>&gt;649</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coke</td>
<td>&gt;C₅₀*</td>
<td>&gt;1000*</td>
<td>&gt;1832*</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Carbon number and boiling point difficult to assess; inserted for illustrative purposes only.
acids are recovered from the alkali washings. The treated oil is further refined and decolorized by adsorption, either by percolation or by contact with clay.

11.3. TEST METHODS

Many test methods are available to determine whether the quality prescribed by consumers for mineral oils is present. In all cases, tests that are carried out for lower-molecular-weight products and for higher-molecular-weight products are of lesser consequence with mineral oil. The stringent methods of refining (purification) remove many of the impurities, of which
ash-forming constituents can be cited as one example, making the test for such constituents redundant. If, for some reason, ash-forming constituents are believed to be present in the mineral oil, the test methods for ash (the presence of ash-forming constituents) that are applied to distillate fuel oil and top residual fuel oil can be applied to mineral oil.

But first, although the importance of careful sampling of any product that is to undergo testing is self-evident, very special precautions must be taken in the case of insulating oils (ASTM D-923, IP 51), for which special techniques are recommended. Precautions that are stipulated are mainly concerned with the avoidance of contamination that would affect electrical tests.

The main requirement of a transformer oil is that it should act as a heat transfer medium to ensure that the operating temperature of a transformer does not exceed acceptable limits. However, the deterioration of transformer oils in service is closely connected with oxidation by air, which brings on deposition of sludge and the development of acids, resulting in overheating and corrosion, respectively (ASTM D-4310). The sludge formed is usually attributed to the direct oxidation of the hydrocarbon constituents to oil-insoluble products.

Mineral oils used as insecticides require measurement of molecular weight (ASTM D-2502, ASTM D-2503, ASTM D-2878) and composition because the structure of the constituents appears to be a factor in determining the insecticide power of these oils. Olefins and aromatics are both highly toxic to insects, but they also have a detrimental effect on plants; thus spray oils generally receive some degree of refining, especially those of the summer oil type that come into contact with foliage.

### 11.3.1. Acidity or Alkalinity

The acid number—the quantity of base, expressed in milligrams of potassium hydroxide per gram of sample, that is required to titrate a sample in this solvent to a green/green-brown end point with p-naphtholbenzein indicator solution (ASTM D-974, IP 139). However, many higher-molecular-weight oil products (dark-colored oils), which cannot be analyzed for acidity because of obscurity of the color-indicator end point, can be analyzed by an alternate test method (ASTM D-664). The quality of the mineral oil products renders them suitable for determination of the acid number.

The principle behind the acid number test is a holdover from earlier refining processes when it was believed, with some justification, that detectable amounts of chemicals that were used in refining could remain in the finished product (ASTM D-974, ASTM D-1093, IP 139). However, oxidation (ASTM D-943, ASTM D-3339, ASTM D-5770, IP 431) of various
oils during use or during storage can induce the formation of acidic species within the oil. Thus the occurrence of acidic entities within the oil is still a concern even though the reason may be different.

To determine the acid number (ASTM D-974), the sample is dissolved in a mixture of toluene and isopropyl alcohol containing a small amount of water, and the resulting single-phase solution is titrated at room temperature with standard alcoholic base or alcoholic acid solution to the end point indicated by the color change of the added \( p \)-naphtholbenzein solution (orange in acid and green-brown in base). To determine the strong acid number, a separate portion of the sample is extracted with hot water and the aqueous extract is titrated with potassium hydroxide solution, with methyl orange as an indicator.

The total absence of organic acidity is never feasible, but a very low limit must be set if corrosion of copper (ASTM D-130, ASTM D-849, ASTM D-4048, ASTM D-4636, IP 154) and other components is to be avoided; moreover, more than a trace of some organic acids can adversely affect the response of the oil to amine inhibitors.

Similarly to the principle of acidic constituents, oil may, on occasion, contain alkaline or basic constituents. The presence of such constituents is determined through test methods for the base number. The relative amounts of these materials can be determined by titrating with acids.

Thus, in a manner akin to the acid number, the base number (often referred to as the neutralization number) is a measure of the basic constituents in the oil under the conditions of the test. The base number is used as a guide in the quality control of oil formulation and is also used as a measure of oil degradation in service.

There are four different test methods for the determination of base numbers (ASTM D-664, ASTM D-974, ASTM D-2896, ASTM D-4739). However, the different base number methods may give different results for the same sample.

If the mineral oil contains additives that react with alkali to form metal soaps, the saponification number (ASTM D-94, IP 136) expresses the amount of base that will react with 1 g of the sample when heated in a specific manner. Because compounds of sulfur, phosphorus, halogens, and certain other elements, which are sometimes added to petroleum products, also consume alkali and acids, the results obtained indicate the effect of these extraneous materials in addition to the saponifiable material present. In the test method, a known weight of the sample is dissolved in methyl ethyl ketone or a mixture of suitable solvents. It is heated with a known amount of standard alcoholic potassium hydroxide for between 30 and 90 min at 80°C (176°F). At the end of the reaction, the excess alkali is titrated with standard hydrochloric acid and the saponification number is calculated.
11.3.2. Aniline Point

The aniline point or mixed aniline point (ASTM D-611, IP 2) gives an indication of the hydrocarbon group composition of an oil. The lower the aniline point, the more aromatic the oil, and, for any particular compound type, the aniline point rises with molecular weight and with viscosity.

In the test, equal volumes of aniline and oil are mixed and heated until a miscible mixture is formed. During cooling at a prescribed rate, the temperature at which the mixture becomes cloudy is recorded and identified as the aniline point. Although not usually applicable to pharmaceutical grade mineral oils, the test is used in technical oil specifications as a measure of degree of refinement and type of base oil stock. For any particular oil fraction, a higher degree of refinement is reflected by an increase in aniline point. Aniline point also increases with the average molecular weight of the oil as well as with increasing proportions of paraffinic hydrocarbons to naphthenic hydrocarbons. Aniline point specifications also can be used to advantage for light technical grade mineral oils used in agricultural sprays, where the presence of aromatic hydrocarbons might cause floral damage.

For electrical oils the aniline point is often an indicator of the aromatic content because too high a value could give rise to oxidation instability and too low a value to inadequate gassing characteristics under electric stress. For these reasons an aniline point, usually in the form of a range of permitted values, is sometimes included in specifications. An increase in the aniline point after extraction with sulfuric acid is perhaps a better indication of aromatic content than the aniline point of the untreated sample.

The test for aniline point (ASTM D-611, IP 2) is not usually applied to medicinal oils, but some users of technical grades specify a minimum value. For oils of similar purity and viscosity a high aniline point denotes a more paraffinic, and hence less dense, oil than a lower aniline point; the desire for a high aniline point runs counter to the view that the higher the density the more preferable the oil if it is desired to make emulsions (e.g., hair cream) therefrom. Generally, the higher the aniline point the greater the stability of the oil but, on the other hand, a high aniline point sample may only indicate more extensive refining if comparisons are made on fractions of the same boiling range from the same crude oil. In addition, variations in aniline point may reflect changes in depth of refining as well as differences in hydrocarbon group composition for oils of same the viscosity but different origins.

11.3.3. Asphaltene Content (Insoluble Constituents)

The asphaltene fraction (ASTM D-893, ASTM D-2006, ASTM D-2007, ASTM D-3279, ASTM D-4124, ASTM D-6560, IP 143) is the highest-
molecular-weight. most complex fraction in petroleum. Insofar as the asphaltene content gives an indication of the amount of coke that can be expected during exposure to thermal conditions (Speight, 2001; Speight and Ozum 2002), there is little need for the application of the test to mineral oil. Thus determination of the asphaltene content of mineral oil may be considered superfluous, but there may be an occasion when there is the need to determine the amount of insoluble constituents precipitated by the addition of a low-boiling hydrocarbon liquid to mineral oil.

In any of the methods for the determination of the asphaltene content, a sample is mixed with a large excess (usually >30 volumes hydrocarbon per volume of sample) of low-boiling hydrocarbon such as \( n \)-pentane or \( n \)-heptane (Speight et al., 1984). For an extremely viscous sample, a solvent such as toluene may be used before the addition of the low-boiling hydrocarbon but an additional amount of the hydrocarbon (usually >30 volumes hydrocarbon per volume of solvent) must be added to compensate for the presence of the solvent. After a specified time, the insoluble material (the asphaltene fraction) is separated (by filtration) and dried. The yield is reported as percentage (% w/w) of the original sample.

Another method is designed to remove pentane-insoluble constituents by membrane filtration (ASTM D-4055). In this method, a sample of oil is mixed with pentane in a volumetric flask, and the oil solution is filtered through a 0.8-\( \mu \)m membrane filter. The flask, funnel, and filter are washed with pentane to completely transfer any particulates onto the filter, after which the filter (with particulates) is dried and weighed to give the pentane-insoluble constituents as a percentage by weight of the sample.

The precipitation number is often equated to the asphaltene content, but there are several issues that remain obvious in its rejection for this purpose. For example, the method to determine the precipitation number (ASTM D-91) advocates the use of naphtha for use with black oil or lubricating oil and the amount of insoluble material (as a % v/v of the sample) is the precipitating number. In the test, 10 ml of sample is mixed with 90 ml of ASTM precipitation naphtha (which may or may nor have a constant chemical composition) in a graduated centrifuge cone and centrifuged for 10 min at 600–700 rpm. The volume of material on the bottom of the centrifuge cone is noted until repeat centrifugation gives a value within 0.1 ml (the precipitation number). Obviously, this can be substantially different from the asphaltene content.

11.3.4. Carbonizable Substances (Acid Test)

Medicinal oil requires a test in which the reaction of the oil to hot, strong sulfuric acid is used to determine the presence of carbonizable substance in the oil. However, the test for carbonizable substances (ASTM D-565)

In the test method (ASTM D-565), the mineral oil is treated with concentrated sulfuric acid under prescribed conditions and the resulting color is compared with a reference standard to determine whether it passes or fails the test. When the oil layer shows no change in color and when the acid layer is not darker than the reference standard colorimetric solution, the oil is reported as passing the test. A bluish haze or a slight pink or yellow color in the oil layer should not be interpreted as a change in color. This is a pass-fail, and the more fully refined the oil, the lighter the color of the acid layer.

With the introduction of ultraviolet absorption procedures (ASTM D-2008, ASTM D-2269), the test finds less use but still provides a useful method to determine possible contamination of mineral oil with impurities transparent to both visible and ultraviolet light and hence not detectable by color or by ultraviolet absorption measurements.

For technical mineral oils the test for unsulfonatable residue (ASTM D-483) may be applied, but the test is of less significance for mineral oil that is refined to medicinal standard. The other quality criteria are much more stringent, and the test method for unsulfonatable residue does not have the required sensitivity.

11.3.5. Carbon Residue

Mineral oils are usually considered to have a high propensity for carbon formation and deposition under thermal conditions. Nevertheless, the tests that are applied to determine the carbon-forming propensity of fuel oil (and other petroleum products) are also available for application to mineral oils. The test methods for the carbon residue should not be confused with the test method for carbonizable substances (ASTM D-565). The former test methods are thermal in nature, whereas the latter test method involves the use of sulfuric acid in a search for specific chemical entities within the oil.

Thus the tests for Conradson carbon residue (ASTM D-189, IP 13), the Ramsbottom carbon residue (ASTM D-524, IP 14), the microcarbon carbon residue (ASTM D4530, IP 398), and asphaltene content (ASTM D-893, ASTM D-2006, ASTM D-2007, ASTM D-3279, ASTM D-4124, ASTM D-6560, IP 143) are often included in inspection data for fuel oil.

In the Conradson carbon residue test (ASTM D-189, IP 13), a weighed quantity of sample is placed in a crucible and subjected to destructive distillation for a fixed period of severe heating. At the end of the specified heating period, the test crucible containing the carbonaceous residue is cooled in a desiccator and weighed and the residue is reported as a percentage (% w/w) of the original sample (Conradson carbon residue). In the
Ramsbottom carbon residue test (ASTM D-524, IP 14), the sample is weighed into a glass bulb that has a capillary opening and is placed into a furnace (at 550°C/1022°F). The volatile matter is distilled from the bulb, and the nonvolatile matter that remains in the bulb cracks to form thermal coke. After a specified heating period, the bulb is removed from the bath, cooled in a desiccator, and weighed to report the residue (Ramsbottom carbon residue) as a percentage (% w/w) of the original sample. In the microcarbon residue test (ASTM D4530, IP 398), a weighed quantity of the sample placed in a glass vial is heated to 500°C (932°F) under an inert (nitrogen) atmosphere in a controlled manner for a specific time and the carbonaceous residue [carbon residue (micro)] is reported as a percentage (% w/w) of the original sample.

The data produced by the microcarbon test (ASTM D-4530, IP 398) are equivalent to those produced by the Conradson carbon method (ASTM D-189, IP 13). However, this microcarbon test method offers better control of test conditions and requires a smaller sample. Up to 12 samples can be run simultaneously. This test method is applicable to petroleum and to petroleum products that partially decompose on distillation at atmospheric pressure and is applicable to a variety of samples that generate a range of yields (0.01% w/w to 30% w/w) of thermal coke.

The data give an indication of the amount of constituents that may be undesirable in the oil, thereby requiring that the oil, depending on its designated use, be subjected to further refining.

Finally, a method that is used to determine pitch volatility (ASTM D-4893) might also be used, on occasion, to determine the nonvolatility of mineral oil. In the method, an aluminum dish containing about 15 g of accurately weighed sample is introduced into the cavity of a metal block heated and maintained at 350°C (662°F). After 30 min, during which the volatiles are swept away from the surface of the sample by preheated nitrogen, the residual sample is taken out and allowed to cool down in the desiccator. Nonvolatility is determined by the sample weight remaining and reported as % w/w residue.

### 11.3.6. Cloud Point

The cloud point is the temperature at which a cloud of wax crystal first appears in a liquid when it is cooled under conditions prescribed in the test method. This test method covers only petroleum oils that are transparent in layers 38 mm (1.5 in.) in thickness, and have a cloud point below 49°C (120°F). The cloud point is an indicator of the lowest temperature of the utility of an oil for certain applications, and it is usually higher than the pour point (ASTM D-97, ASTM D-5853, ASTM D-5949, ASTM D-5950, ASTM D-5985, IP 15).
The cloud point (ASTM D-2500, ASTM D-5771, ASTM D-5772, ASTM D-5773, IP 219) is the temperature at which wax appears in an oil. This information is significant for oils to be used at low temperatures, where precipitation of wax might affect the performance of the oil.

In one of the tests (ASTM D-2500, IP 219), the oil is maintained at 0°C (32°F) for 4 h, when a 0.5-mm black line must be easily seen through an oil layer 25 mm thick. The setting of a value as low as this is dictated largely by considerations of appearance of the oil; a much higher temperature could well be tolerated if only practical considerations applied. Moreover the \( n \)-paraffins that are responsible for cloudiness (hence the need to observe that the opalescence is not due to moisture) are among the more inert of the hydrocarbon groups of which these mineral oils are composed.

The later test methods (ASTM D-5771, ASTM D-5772, ASTM D-5773) are alternative procedures that use automatic apparatus. However, when the specifications state that the original method (ASTM D-2500, IP 219) should be used, these later methods should not be applied without obtaining comparative data first. However, all three methods have a higher degree of precision than the original method.

Neither the cloud point nor the pour point should be confused or interchanged with the freezing point (ASTM D 2386, ASTM D-5901, ASTM D-5972, IP 16, IP 434, IP 435). The freezing point presents an estimate of minimum handling temperature and minimum line or storage temperature. It is not a test for an indication of purity and has limited value for mineral oil.

### 11.3.7. Color and Taste

By definition, pharmaceutical grade mineral oil must be colorless and transparent. Although the eye can determine color, it is usual to determine color by instrument.

The colorless character of these oils is important in some cases, because it may indicate the chemically inert nature of the hydrocarbon constituents. Textile lubricants should be colorless to prevent staining of light-colored threads and fabrics. Insecticide oils should be free of reactive (easily oxidized) constituents so as not to injure plant tissues when applied as sprays (ASTM D-483).

The main use of mineral oil in medicine has been as a laxative (an alimentary tract lubricant) and in various pharmaceutical preparations such as ointments, and, as such use continues, this quality of oil is finding increasing utilization as a lubricant for food processing machinery and in plastics manufacture. Laxative oils should be free of odor and taste and also be free of hydrocarbons that may react during storage and produce unwanted by-products. These properties are attained by the removal of oxygen-,
nitrogen-, and sulfur-containing compounds, as well as reactive hydrocarbons by, for example, sulfuric acid. The maximum permissible quantity of such oil traces is prescribed, but also the purity of the oil (ASTM D-2269) requires that the absorbance be measured on a dimethyl sulfoxide extract of the oil.

Determination of the color of mineral oil is used mainly for manufacturing control purposes and is an important quality characteristic. In some cases the color may serve as an indication of the degree of refinement of the material. However, color is not always a reliable guide to product quality and should not be used indiscriminately in product specifications (ASTM D-156, ASTM D-1209, ASTM D-1500, ASTM D-1544, ASTM D-6045, IP 17).

In one test (ASTM D-156) for the determination of color the height of a column of the oil is decreased by levels corresponding to color numbers until the color of the sample is lighter than that of the standard. The color number immediately above this level is recorded as the Saybolt color of the oil, and a color number of +25 corresponds to water mineral, whereas the minimum color intensity reading on this scale is expressed by +30, a value normally attained by mineral oils. In another test (IP 17), in which the measurements are performed with an 18-in. cell against color slides on a scale, a color of 1.0 or under is considered water-mineral and medicinal oils will normally be 0.5 or less. Conversion scales for different color tests are available (ASTM D-1500).

Although sometimes found in insulating oil specifications, the color characteristic is of no technical significance. Pale oils are, as a general rule, more severely refined than dark oils of the same viscosity, and color (ASTM D-1500, IP 17) is not a guide to stability. Deterioration of color after submission of the oil to an aging test is sometimes limited, but here again extent of oil deterioration can be much better measured by some other property such as acidity development or change in electrical conductivity (ASTM D-2624, ASTM D-4308, IP 274). About the only point that can be made in favor of color measurement on new oil is that it can give an immediate guide to a change in supply continuity.

11.3.8. Composition

The potential for the presence in mineral oil of trace amounts of carcinogenic polynuclear aromatic hydrocarbons cannot be overestimated. Thus compositional tests focus on the production of data relating to the presence of aromatic and polynuclear aromatic constituents in mineral oil.

As a result, a test method (ASTM D-2269) that can be applied to the ultraviolet absorbance of mineral oil is available. The investigation can be performed either directly on the oil itself (or on oil diluted with inert solvent) or else on a solvent extract of the oil, the solvent chosen (e.g.,
dimethyl sulfoxide) being one that will extract and concentrate the polynuclear aromatics.

Although informative, there have also been extensive efforts to correlate composition with physical properties. Among the most definitive of these efforts was the refractive index-density-molecular weight (n-d-M) method (ASTM D-3238). Carbon type composition gives the breakdown of total carbon atoms between various structures. Following from this, another method (ASTM D-2140, derived from n-d-M analysis (ASTM D-3238), involves the measurement of refractive index, density, and viscosity, for all of which standard procedures are available. From the data, it is possible to determine the distribution of carbon types (paraffin chains, naphthenic rings, and aromatic rings) in the oil. However, it is important to recognize that the percent aromatic carbon determined by this method does not correspond to aromatics as determined by other procedures (e.g., adsorption chromatography). For example, octadecylbenzene (C_{6}H_{5}C_{18}H_{37}) has only 25% of the carbon as aromatic carbon (C_{A}) but chromatographic separation would show this compound to be separated as an aromatic compound.

Aniline point (ASTM D-611, IP 2) gives an indication of the hydrocarbon group composition of oil. The aniline point rises with molecular weight; also, for a given viscosity, the higher the aniline point the more paraffinic the oil. For electrical oils it is sometimes desirable to control the aromatic content because too high a value could give rise to oxidation instability and too low a value to inadequate gassing characteristics under electric stress. For these reasons an aniline point, usually in the form of a range of permitted values, is sometimes included in specifications. And a rise in the aniline point after extraction with sulfuric acid is perhaps a better indication of aromatic content than aniline point on the untreated sample.

A technique for applying infrared measurements to insulating oil is available (ASTM D-2144), and considerable information about mineral oil composition can be gained from infrared spectroscopy. Oxygenated bodies formed when oil deteriorates can be recognized, and hence this procedure can be used for surveillance of oils in service. An infrared spectrum can also give information as to the aromaticity of an oil and can detect antioxidants such as 2,6 di-tertiary butyl p-cresol. A chemical test for the latter is, however, available and is preferable for quantitative purposes (ASTM D-1473).

Although the total sulfur content (ASTM D-129, IP 61) of medicinal oil is not limited as such, it is in effect restricted (usually to well below 100 ppm) by the necessity of severe refining to meet the other clauses of the specification. However, the total sulfur content of mineral oils normally is well below 100 ppm because of the severe refining to which the oil has been subjected (Speight, 2000). Therefore, sulfur is not a limiting factor in the
specifications of mineral oil. Nevertheless, test methods are available to determine the presence of sulfur compounds in mineral oil, although the preferred procedure is often the Doctor test (ASTM D-4952, IP 30). For medicinal oils the procedure is that two drops of a saturated solution of lead monoxide in 20% aqueous sodium hydroxide are added to two volumes of oil and one volume of absolute ethyl alcohol. The mixture is heated to 70°C (158°F) for 10 min and should remain colorless.

Other test methods for the determination of corrosive sulfur (specifically hydrogen sulfide) are also available (ASTM D-6021, ASTM D-5705), which have been developed for residual fuel oil but can be applied to medicinal oil. Another test method (ASTM D-3227, IP 324) is used for the determination of mercaptan (R-SH) sulfur in petroleum products up to and including distillate fuels. However, there is no reason that the test could not be applied to mineral oil, with the use of any necessary modifications for solubility of the mineral oil in the alcoholic solution used for the titration.

In view of the wide use of copper in electrical equipment, it is essential to ensure that the oil does not corrode this metal. Noncorrosive or corrosive sulfur can be verified by any one of several test methods (ASTM D-130, ASTM D-849, ASTM D-4048, ASTM D-4636, IP 154) in which the oil is heated in the presence of a metallic copper strip for a specified time at a specified temperature after which the strip must be discolored. In addition, corrosiveness toward silver is becoming increasingly important, and a test method (IP 227) has been developed that is closely similar to the copper corrosion test.

Molecular type analysis separates an oil into different molecular species. A molecular type analysis is the so-called *clay-gel analysis*. In this method, group separation is achieved by adsorption in a percolation column with selected grades of clay and silica gel as the adsorption media (ASTM D-2007).

### 11.3.9. Density (Specific Gravity)

The use of density (specific gravity) data (ASTM D-1298, IP 160) for mineral oil is variable, although, for some grades of mineral oil, a high density can be indicative of the ultimate use of the oil.

For example, density or specific gravity data (ASTM D-1298, ASTM D-1480, ASTM D-1481, ASTM D-4052, ASTM D-5002 IP 160) are frequently included as a specification requirement for transformer oil when transformers operate in cold climates. Water, however undesirable in electrical equipment, does collect therein, and if an oil has a high density, any water/ice present would float on the oil instead of remaining at the bottom of the oil container, thereby reducing the effectiveness of the oil.
For heavier insulating oil, the purpose of limiting density range is to provide a check on oil composition. In addition, a minimum density may offer some indication of solvent power as well as guarding against excessive paraffin content. In this respect, the inclusion of density in a mineral oil specification may duplicate the aniline point (ASTM D-611, IP 2) requirement.

The API gravity (ASTM D-287) is a special function of specific gravity that was arbitrarily established to permit use of a wider industrial range of numbers and is derived from the specific gravity:

\[
\text{API gravity, deg} = (141.5/\text{sp gr } 60/60\degree F) - 131.5
\]

Density, specific gravity, and API gravity values permit conversion of volumes at the measured temperature to volumes at the standard petroleum temperatures of 15°C (60°F). Calculation of weight is possible where compositions are formulated on a weight basis. At a given viscosity, density, specific gravity, and API gravity provide a means for determining whether a mineral oil is derived from a paraffinic or a naphthenic feedstock.

### 11.3.10. Electrical Properties

Electrical properties of one form or another are included in virtually all specifications for insulating oils.

The electric strength or dielectric breakdown test method (ASTM D-877) indicates the absence, or presence, of free or suspended water and other contaminant matter that will conduct electricity. A high electric strength gives no indication of the purity of an oil in the sense of degree of refinement or the absence of most types of oil-soluble contaminants. This test method is of some assistance, when applied to an otherwise satisfactory oil, to indicate that the oil is free of contaminants of the type indicated above; in practice, this ensures that the oil is dry.

The test for stability (gas evolution) under electric stress must not be confused with tests for the gas content of insulating oil (ASTM D-831, ASTM D-1827, ASTM D-2945). These tests are largely factory control tests to ensure that oils intended for filling equipment have been adequately degassed (because dissolved gas, like gas evolved under stress, could cause void formation).

### 11.3.11. Flash Point and Fire Point

The flash point (closed tester: ASTM D-93/IP 34; open tester: ASTM D-92/IP 36) is the lowest temperature at atmospheric pressure (760mmHg, 101.3kPa) at which application of a test flame will cause the vapor of a
sample to ignite under specified test conditions. The sample is deemed to have reached the flash point when a large flame appears and instantaneously propagates itself over the surface of the sample. Flash point data are used in shipping and safety regulations to define flammable and combustible materials. Flash point data can also indicate the possible presence of highly volatile and flammable constituents in a relatively nonvolatile or nonflammable material. The fire point (ASTM D-92, IP 36) is the temperature at which the oil ignites and burns for 5 s.

Of the available test methods (ASTM, 2000), the most common method of determining the flash point confines the vapor (closed cup) until the instant the flame is applied (ASTM D-56, ASTM D-93, ASTM D-3828, ASTM D-6450, IP 34, IP 94, IP 303). An alternate method that does not confine the vapor (open cup method (ASTM D-92, ASTM D-1310, IP 36) gives slightly higher values of the flash point.

The flash point is sometimes to be found in a mineral oil specification, but the value is not usually of much significance and is merely laid down as some assurance against undue fire risk. Typical values will be from 150°C (302°F) upward, depending on viscosity. The closed test (IP 34) is commonly used, and a minimum value of 140°C (284°F) is required for transformer oil to limit fire risk. The stipulation of a suitable flash point also automatically limits the volatility of the oil, and for this reason the loss on heating (IP 46) can be important to restrict excessive volatility. This can be achieved by setting a suitable minimum flash point on the order of 125°C (257°F).

Fewer volatility problems arise with the heavier cable oils or oil-based cable impregnating compounds, although here also a minimum flash point of approximately 230°C (446°F) is frequently specified as a precaution against the presence of lighter (and hence undesirably volatile) components that could be troublesome at impregnating conditions of over 100°C (212°F) and high vacuum.

Rubber compounders often use flash point (ASTM D-92, IP 36, ASTM D 93, IP 34) as a measure of oil volatility. Volatility is important because rubber products are exposed to elevated temperatures during mixing operations and, often, in service. Although flash point has a certain utility for this purpose, it gives no indication of the amount of low-boiling material present. Therefore, a distillation curve should be used when volatility is a critical factor.

### 11.3.12. Interfacial Tension

The measurement of interfacial tension (ASTM D-971, ASTM D-2285) between oil and water is a sensitive method for determining traces of polar contaminants, including products of oil oxidation, and minimum values will sometimes be found in insulating oil specifications. The test is frequently...
used to assess transformer oil deterioration and thus to maintain a check on the quality of oil in electrical equipment.

### 11.3.13. Iodine Value

The iodine number (iodine value) test method (ASTM D-2078, IP 84) is included in some specifications and is a measure of fatty acid components or unsaturation either as olefins and/or aromatics. The former are very unlikely to be present in any oil that has undergone sufficient refining to make it colorless, whereas the aromatic content can be controlled by setting a suitable value for the ultraviolet absorption.

In the test method (ASTM D-2078), a sample is dissolved in chloroform and reacted with Wijs solution for 30 min in the dark at 25°C. At the end of the reaction, the solution is mixed with potassium iodide (KI) and titrated with sodium thiosulfate and starch indicator and compared to a blank determination.

The bromine number is the number of grams of bromine that will react with 100 g of the sample under the test conditions and is better suited to the determination of unsaturated constituents in oil (ASTM D-875, ASTM D-1159, ASTM D-2710, IP 130). The magnitude of the bromine number is used as a measure of aliphatic unsaturation in petroleum products. In the test, a known weight of the sample dissolved in a specified solvent maintained at 0–5°C (32–41°F) is titrated with standard bromide-bromate solution. Determination of the end point is method dependent.

### 11.3.14. Oxidation Stability

Very many oxidation tests for transformer oils have been used at one time or another. Most of these tests are of a similar pattern: The oil is heated and subjected to oxidation by either air or oxygen and usually in the presence of a metallic catalyst, almost invariably copper, which is the main active metal in transformer construction. Temperatures and duration have varied within wide limits, from 95 to 150°C (203–302°F) and from 14 to 672 h.

In one test method (ASTM D-943), the oil is maintained at 100°C (212°F) for up to 1 week, during which time oxygen is passed through the oil, in which metallic copper is immersed. At the end of the oxidation period the amount of solid deterioration products (sludge) is measured, after such sludge has been precipitated by dilution of the aged oil with *n*-heptane, and the soluble (acid) decomposition products are also measured by determination of the neutralization value of the aged oil.

To shorten the time for the oxidation test method, a test for sludge formation in transformer oil by high-pressure oxidation bomb has been deve
oped (ASTM D-1313) in which oxidation is carried out at 140°C (284°F) under pressurized oxygen for 24 h and the sludge formed is separated and weighed. A somewhat similar test, designed for inhibited oils, operates at the same temperature but lower pressure and employs a copper catalyst (ASTM D-2112).

One criticism of such tests is that sludge precipitation is carried out with precipitation naphtha. Although the characteristics of this mixture are defined, it is a complex hydrocarbon mixture whose composition can vary widely even within the range of prescribed properties. This could give rise to varying precipitation capabilities in various batches of such naphtha, a disadvantage that cannot occur when a pure chemical such as n-heptane is used as precipitant (ASTM D-3279, ASTM D-4124, IP 143). Another criticism is that the pressurized oxygen might be capable of changing the chemistry of the oxidation reaction and that the oxidation conditions do not represent the service conditions.

Although most transformer oil oxidation tests are of the air- or oxygen-blowing type, many methods of assessing cable oil deterioration depend on static oxidation, that is, the oil and air are in contact but such contact is not stimulated. A catalyst is sometimes, but not invariably, used. Thus, in the open beaker oxidative aging test (ASTM D-I934), the oil is exposed to moving air at 115°C (239°F) for 96 h but a metallic catalyst is optional. The metal is not specified, although copper is most frequently used in oxidation tests on insulating oils. Characteristics to be determined after aging are again left open in the test description, although acidity and electrical conductivity (both AC and DC) are the most common. Color is sometimes included, but the limited amount of information that this conveys has already been commented upon.

A transformer oil should not contain levels of unsaturated components (aromatics and/or olefins) that affect the oxidation resistance of the oil (ASTM D-2300). Another type of test (ASTM D-2298) exposes the degassed oil to electric stress, in a vacuum and at room temperature, the amount of gas evolved at the end of 1000 min being measured.

Acidity (ASTM D-974, IP 1, IP 139) after oxidation is another criterion by which the extent of oil deterioration is judged.

11.3.15. Pour Point

The pour point provides a means of determining the type of petroleum feedstock from which the mineral oil was manufactured or its previous processing history. It also reflects the presence of wax or paraffinic hydrocarbons. In any application in which the mineral oil is used at low temperatures or the oil is subjected during handling or storage to low temperatures, the pour point is important and, perhaps, even critical.
In the pour point test (ASTM D-97, IP 15), the oil is heated to a specified temperature that is dependent on the anticipated pour point range, cooled at a specified rate, and examined at 3°C (5°F) intervals for flow. The lowest temperature at which no movement of the oil is detected is recorded. The 3°C (5°F) temperature value immediately preceding the recorded temperature is defined as the pour point.

For the pour point of transformer oils, a value below the lowest ambient temperature to be expected must be set according to the specifications. Most oils have a pour point that is typically on the order of –40°C (–40°F).

11.3.16. Refractive Index

The refractive index (ASTM D-1218, ASTM D-1747) is the ratio of the velocity of light in air to its velocity in the substance under examination. It is used, together with density and viscosity measurements, in calculating the paraffin-naphthenic ratio in mineral oils. Because refractive index is a measure of aromaticity and unsaturation on a given stock, manufacturers also use it as a means of process control.

The refractive index is also needed to calculate the refractivity intercept in the determination of carbon type composition (Speight, 2000).

11.3.17. Smoke Point

The smoke point is of particular interest to industries, such as the baking industry, whose processes expose or use mineral oil at extremely high temperatures.

The smoke point test (ASTM D-1322, IP 57), originally developed for kerosene, is conducted with an enclosed wick-fed lamp suitably vented and illuminated to permit detection of vapors. The oil is carefully heated under specified conditions until the first consistent appearance of vapors is detected. The temperature of the oil at that time is recorded as the smoke point. If necessary, this test can be adapted for use with mineral oil. The character of the flame is an indicator of the aromatics content.

11.3.18. Specific Optical Dispersion

The specific optical dispersion (ASTM D-1807) serves as an indication of aromatic content. The difference in refractive index of the oil as measured at two wavelengths is determined, divided by the relative density (all measurements are at the same temperature) and multiplied by 100; values above 97 are stated to bear a direct relationship to the aromatic content of the oil.

If, however, there is reason to be particularly interested in the aromatic content, it is preferable to assess this by one of the more direct methods.
11.3.19. Ultraviolet Absorption

Considerable concern has been generated in recent years over the possible presence of carcinogenic polynuclear aromatic hydrocarbons in mineral oils.

Detection of these chemicals by ultraviolet absorption spectroscopy (ASTM D-2269) measures the absorbance over the wavelength range of 260–350 nm in a 10-mm cell of a dimethyl sulfone extract of the oil. The polynuclear aromatic hydrocarbons present in the mineral oils are concentrated. In fact, the ultraviolet absorption level corresponds, approximately, to a maximum polynuclear aromatics content of about 5 ppm.

For oils of a similar type, ultraviolet (UV) absorptivity is a good indicator of the resistance of an oil to discoloration under exposure to artificial or natural light. Oils with low absorptivity at 260 nm have been found to impart good color stability to light-colored rubber compounds (ASTM D-2008).

11.3.20. Viscosity

Viscosity (ASTM D-445, IP 71) is one of the most important properties to be considered in the evaluation of a mineral oil.

Requirements for viscosity vary widely according to the user for which the oil is intended and may be as low as 4 cSt or as high as 70 cSt. Mineral oil for internal use generally should have high viscosity to minimize possibilities of leakage.

Viscosity data (ASTM D-445, IP 71) are used to ensure that, in the case of oils for internal use as laxatives, unduly fluid material, which could increase risk of leakage through the anal sphincter muscle, is not used. The minimum viscosity is usually on the order of 75 cSt at 37.8°C (100°F). The temperature of viscosity measurement is a normal one employed for this purpose and happens, in the case of medicinal oils, to be that of the human body. Thus the viscosity of these oils is measured at their working temperature.

Heavy cable oils are very much more viscous materials, and typical viscosity values can be as high as about 200 cSt at 60°C (140°F). Such oils are probably the only petroleum products for which a maximum viscosity index (ASTM D-227, IP 226) is sometimes specified, to ensure that, although the oil will be as fluid as possible at impregnating temperatures (100°C/212°F or more), it will be sufficiently viscous to prevent draining at ambient temperatures in cases where cables are laid on a steep gradient.

The viscosity-gravity constant (ASTM D-2501) and the refractivity intercept (r) have been used for characterizing oils of widely different viscosity (ASTM D-2140).
11.3.21. Volatility

The distillation range for very mineral light oils provides information on volatility, evaporation rates, and residue remaining after evaporation (ASTM D-86, ASTM D-1160, IP 123).

Such data are important for agricultural and household sprays, agricultural product processing, and printing inks. The baking and plastic industries often include initial boiling point temperature, the minimum allowable temperature at which the first several percent of the oil comes overhead during distillation, or both as part of their specifications for mineral oils.

The test for evaporation (ASTM D-972) gives a measure of oil volatility under controlled conditions and is used frequently for specification purposes. However, because volatility of oil from a rubber compound may be influenced by its compatibility with the rubber, a volatility test of the compound often is made under laboratory test conditions pertinent to the intended service.

11.3.22. Water

Water is obviously undesirable in electrical equipment, and the water content of transformer and other insulating oils is frequently limited to a low maximum value. Traces of water that would not influence the general run of petroleum product tests could have a very significant effect on properties such as electric strength.

Quantitative determination may be made by one of the many modifications of the Karl Fischer method (ASTM D-1533). With careful application of this technique, using electrical methods of determining the end point and operating in a sealed system, water can be determined down to about 2 ppm or even less. Such sensitivity is, however, rather greater than is normally required, and a water content of 35 ppm and preferably less than say 25 ppm is usually considered satisfactory. The solubility level of water in oil at room temperature (say 20°C/68°F) will vary with the type of oil but is around 40 ppm. Amounts of water down to about 5 ppm, in addition to being measurable chemically, can also be determined by removing the water from the oil by a combination of heat and vacuum and absorbing the freed moisture in a suitable weighed phosphorus pentoxide (P$_2$O$_5$) trap.

11.3.23. Wax Appearance Point

The wax appearance point is the temperature at which wax begins to precipitate (hence it is also called the wax precipitation point) from an oil under specified cooling conditions. Although more applicable to distillate fuel oil, the wax appearance point can also have implications for mineral oil use. In
the test method (ASTM D-3117), a sample of the oil is cooled under pre-
scribed conditions with stirring. The temperature at which wax first appears
is the wax appearance point.

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