



## Standard Test Methods for Analysis of Lubricating Grease<sup>1</sup>

This standard is issued under the fixed designation D 128; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of the Department of Defense.*

<sup>e1</sup> NOTE—Warning notes were editorially moved into the standard text in July 2003.

### 1. Scope

1.1 These test methods for analysis cover greases of the conventional type, which consist essentially of petroleum oil and soap. The constituents that can be determined are soap, unsaponifiable matter (petroleum oil, and so forth), water, free alkalinity, free fatty acid, fat, glycerin, and insolubles.

NOTE 1—Any of the test methods described herein are best used by an experienced grease analyst who may also be able to make appropriate adaptations of the techniques as occasion requires.

1.2 A supplementary test method is provided in Appendix X1. This test method is intended primarily for application to greases containing thickeners that are essentially insoluble in *n*-hexane, and to greases that cannot be analyzed by conventional methods because of the presence of such constituents as nonpetroleum fluids or nonsoap-type thickeners, or both. In some cases, these constituents can react with strong acid or alkaline solutions.

1.3 These test methods appear in the following order:

	Sections
Ash Determination	7-11
Insolubles, Soap, Fat, Petroleum Oil, and Unsaponifiable Matter	12-20
Free Alkali and Free Acid	21-23
Water	24
Glycerin (Quantitative)	25-29

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices, and determine the applicability of regulatory limitations prior to use.*

1.5 The values stated in SI units are to be regarded as the standard.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

D 95 Test Method for Water in Petroleum Products and

Bituminous Materials by Distillation<sup>2</sup>  
D 156 Test Method for Saybolt Color of Petroleum Products (Saybolt Chromometer Method)<sup>2</sup>  
D 217 Test Methods for Cone Penetration of Lubricating Grease<sup>2</sup>  
D 445 Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (the Calculation of Dynamic Viscosity)<sup>2</sup>  
D 473 Test Method for Sediment in Crude Oils and Fuel Oils by the Extraction Method<sup>2</sup>  
D 1078 Test Method for Distillation Range of Volatile Organic Liquids<sup>3</sup>  
D 1193 Specification for Reagent Water<sup>4</sup>  
D 1353 Test Method for Nonvolatile Matter in Volatile Solvents for Use in Paint, Varnish, Lacquer, and Related Products<sup>3</sup>

### 3. Terminology

#### 3.1 Definitions:

3.1.1 *asphalt, n*—a dark brown-to-black cementitious material in which the predominating constituents are bitumens.

3.1.1.1 *Discussion*—Asphalt can be a natural product or a material obtained from petroleum processing.

3.1.2 *candle pitch, n*—a dark brown-to-black, tarry or solid, by-product residue from soap and candle stock manufacture, refining of vegetable oils, refining of wool grease, or refining of refuse animal fats.

3.1.3 *cup grease, n*—any lubricating grease having physical properties, such as consistency and texture, suitable for its use in spring-loaded or screw-type lubricating cups.

3.1.3.1 *Discussion*—Cup greases are predominantly NLGI No. 3 or 4 calcium greases, but grease types other than calcium are also used.

3.1.4 *degras (wool fat, wool grease, wool wax), n*—a fat-like material comprised primarily of sterols, other higher alcohols, and fatty acids, obtained from the solvent extraction of sheep's wool.

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and are the direct responsibility of Subcommittee D02.G0 on Lubricating Grease.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 05.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 06.04.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 11.01.

3.1.5 *free alkali, n*—in lubricating grease, unreacted basic (alkaline) material present in the product.

3.1.5.1 *Discussion*—Many greases are made with a slight excess of alkali to ensure complete saponification. Free alkali is determined by acidification of a solvent-thinned specimen and back titration with standardized, alcoholic potassium hydroxide. It is expressed in terms of the predominating alkali and a mass % of the total grease composition (for example, mass % lithium hydroxide).

3.1.6 *free fatty acid, n*—in lubricating grease, unreacted carboxylic acid(s) present in the product.

3.1.6.1 *Discussion*—Some greases are made with a slight excess of carboxylic acid to ensure a non-alkaline product. Free fatty acid is determined by neutralization of a solvent-thinned specimen with standardized, alcoholic potassium hydroxide. Regardless of the actual composition of the carboxylic acid(s), it is expressed as free oleic acid and as a mass % of the total grease composition.

3.1.7 *insolubles, n*—in lubricating greases analysis, the material remaining after the acid hydrolysis, water extraction, and solvent extraction of soap-thickened greases.

3.1.7.1 *Discussion*—Consisting of such products as graphite, molybdenum disulfide, insoluble polymers, and so forth.

3.1.8 *lubricating grease, n*—a semi-fluid to solid product of a dispersion of a thickener in a liquid lubricant.

3.1.8.1 *Discussion*—The qualifying term, *lubricating*, should always be used. The term, *grease*, used without the qualifier refers to a different product, namely certain natural or processed animal fats, such as tallow, lard, and so forth.

3.1.9 *mixed base, adj*—in lubricating grease, the description of a thickener system composed of soaps of two metals.

3.1.9.1 *Discussion*—Although mixed-base grease can be made with soaps of more than two metals, in practice, such is rarely, if ever, encountered. All of the soaps need not be thickeners, although the major soap constituent will be one capable of forming a lubricating grease structure. Because the mixed soaps are seldom present in equal amounts. The predominant soap is referred to first.

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3.1.10 *montan wax, n*—a wax-like material comprised primarily of montanic acid and its ester, higher aliphatic alcohols, and resins obtained from the solvent extraction of lignite.

3.1.11 *neutralization number, n*—of petroleum oil, the quantity of acid or base required to titrate to neutrality and expressed as equivalent milligrams of potassium hydroxide per gram of sample. **D 804**

3.1.12 *NLGI, n*—National Lubricating Grease Institute.

3.1.13 *NLGI number, n*—a numerical scale for classifying the consistency range of lubricating greases and based on the Test Methods D 217 worked penetration.

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3.1.14 *non-soap thickener (synthetic thickener, inorganic thickener, organic thickener), n*—in lubricating grease, any of several specially treated or synthetic materials, excepting metallic soaps, that can be thermally or mechanically dispersed

in liquid lubricants to form the lubricating grease structure.

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3.1.15 *residuum, n*—a liquid or semi-liquid product obtained as residue from the distillation of petroleum and consisting primarily of asphaltic hydrocarbons.

3.1.15.1 *Discussion*—Also known as asphaltic oil, asphaltum oil, liquid asphalt, black oil, petroleum tailings, and residual oil.

3.1.16 *rosin oil, n*—a viscous, oily liquid obtained as a condensate when the residue (rosin) from turpentine production is subjected to dry, destructive distillation.

3.1.16.1 *Discussion*—Also used to describe specially compounded oils having a rosin base.

3.1.17 *saponification, n*—the interaction of fats, fatty acids, or esters generally with an alkali to form the metallic salt, which is commonly called soap.

3.1.17.1 *Discussion*—Soap thickeners are most often made by in situ saponification in the lubricating grease base oil. However, the use of pre-formed soaps is also common; dispersion is effected by mechanical means and usually with heat.

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3.1.18 *single base, adj*—in lubricating grease, relating to a thickener comprised of soaps of only one metal.

3.1.19 *soap, n*—in lubricating grease, a product formed in the saponification (neutralization) of fats, fatty acids, or esters by inorganic bases.

3.1.20 *Soxhlet apparatus, n*—a device, usually of glass, used to extract soluble material from a mixture of soluble and insoluble (generally solid) materials, by passing a volatile solvent through the sample and recirculating the solvent by refluxing.

3.1.21 *tar, n*—a brown or black, bituminous, liquid or semi-solid comprised primarily of bitumens condensed in the processing of coal, petroleum, oil-shale, wood, or other organic materials.

3.1.22 *thickener, n*—in lubricating grease, a substance composed of finely divided solid particles dispersed in a liquid lubricant to form the product's structure.

3.1.22.1 *Discussion*—The thickener can be fibers (such as various metallic soaps) or plates or spheres (such as certain non-soap thickeners), which are insoluble or, at most, only very slightly soluble in the liquid lubricant. The general requirements are that the solid particles be extremely small, uniformly dispersed, and capable of forming a relatively stable, gel-like structure with the liquid lubricant. **D 217**

3.1.23 *thimble, n*—in Soxhlet apparatus, a closed-end porous cylinder used to hold the material to be extracted, usually made of thick matted filter paper but sometimes made of ceramic.

3.1.24 *total fluid constituent, n*—in lubricating grease analysis, the *n*-hexane-soluble material extracted from the lubricating grease sample.

3.1.24.1 *Discussion*—Typical materials include petroleum oil, non-petroleum fluid, soluble fats, and soluble additives.

3.1.25 *total n-hexane-insoluble material, n*—in lubricating grease analysis, that portion of grease (excluding free alkali) that is essentially insoluble in *n*-hexane.

<sup>5</sup> Available from National Lubricating Grease Institute, 4635 Wyandotte St., Kansas City, MO 64112-1596.

3.1.25.1 *Discussion*—Typical materials include thickeners, fillers, inorganic salts, asphaltenes, or any combinations of these (also includes insoluble materials found in the analysis of contaminated grease). Free alkali content is generally insignificant.

3.1.26 *unsaponifiable matter, n—in lubricating grease*, organic materials, either added or found with fatty materials, which do not react during saponification.

#### 4. Significance and Use

4.1 These test methods can be used to identify and estimate the amount of some of the constituents of lubricating greases. These test methods are applicable to many, but not all, greases.

4.2 Composition should not be considered as having any direct bearing on service performance unless such correlation is established.

NOTE 2—Details on other test methods for grease analysis can be found in other reference material.<sup>6,7,8</sup>

#### 5. Reagents

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>9</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type III.

5.3 *Acetone*—American Chemical Society Reagent Grade Acetone. (**Warning**—Extremely flammable. Vapors may cause flash fires.)

5.4 *Alcohol (50 %)*—The alcohol shall be prepared from commercial 95 % ethanol or denatured alcohol<sup>10,11</sup> (**Warning**—Flammable. Denatured. Cannot be made non-toxic) by distilling from NaOH and neutralizing exactly with NaOH or KOH using phenolphthalein as the indicator. (**Warning**—In addition to other precautions, avoid skin contact or ingestion.) Dilute with an equal volume of water.

<sup>6</sup> Stanton, G. M., "Examination of Grease by Infrared Spectroscopy," *NLGI Spokesman*, Vol 38, No. 5, August 1974, pp 153–165.

<sup>7</sup> Stanton, G. M., "Grease Analysis, a Modern Multitechnique Approach," Preprint NLGI Annual Meeting, Oct 26–29, 1975.

<sup>8</sup> Bonomo, F. S., and Schmidt, J. J. E., "Development of Schematic Analytical Procedures for Synthetic Lubricants and Their Additives," *WADC Technical Report 54-464*, Part IV, July 1957 (U.S. Government No. AD-130922).

<sup>9</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

<sup>10</sup> The sole source of supply of denatured grain alcohol known to the committee at this time is Formulas 1, 23-A, 30, and 35-A, as described in Publication No. 368, "Formulas for Denatured Alcohol," U.S. Treasury Dept., Internal Revenue Service.

<sup>11</sup> If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,<sup>1</sup> which you may attend.

TABLE 1 Physical Requirements of *n*-hexane

Test	Requirement	ASTM Designation <sup>A</sup>
Initial boiling point, min, °C	66.1	D 1078
Dry point, max, °C	68.9	D 1078
Nonvolatile matter, max, g/100 mL	0.001	D 1353
Color, Saybolt, min	+ 30	D 156
Reaction with alkalis	<sup>A</sup>	...

<sup>A</sup> Boil 125 mL of *n*-hexane with 10 mL of 0.5 *N* alcoholic KOH solution and 50 mL of neutral 50 % alcohol for 1½ h on a hot plate. Use a glass tube about 7 mm in inside diameter and 750 mm in length as a reflux condenser. After cooling, titrate the solutions with 0.5 *N* HCl using phenolphthalein as the indicator. Not less than 9.8 mL of 0.5 *N* HCl shall be required for neutralization. The amount of alkali consumed in this test shall be deducted as a blank correction in the fat determination on Solution E.

5.5 *Ammonium Carbonate*—(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>. (**Warning**—Harmful if swallowed.) (**Warning**—Harmful if swallowed.)

5.6 *Butter Yellow Indicator* (0.02 g/mL)—Toluene solution (**Warning**—Flammable. Vapor harmful) of *p*-dimethylaminoazobenzene. (**Warning**—Suspected carcinogen. In addition to other precautions, avoid inhalation or skin contact.)

5.7 *t-Butyl Alcohol*, melting point 24 to 25.5°C (**Warning**—Flammable liquid; causes eye burns).

5.8 *Carbon Disulfide* (CS<sub>2</sub>). (**Warning**—Extremely flammable. Poison. Vapor may cause flash fire. Vapor harmful. Capable of self-ignition at 100°C or above. Harmful or fatal if swallowed. May be absorbed through the skin.)

5.9 *Ethyl Ether*. (**Warning**—Extremely flammable. Harmful if inhaled. May cause eye injury. Effects may be delayed. May form explosive peroxides. Vapors may cause flash fire. Moderately toxic. Irritating to skin.)

5.10 *n-hexane*, high-purity grade,<sup>11,12</sup> conforming to the requirements of Table 1. (**Warning**—Extremely flammable. Harmful if inhaled. May produce nerve cell damage. Vapors may cause flash fire.)

5.11 *Hydrochloric Acid* (37 %)—Concentrated acid (HCl). (**Warning**—Poison. Corrosive. May be fatal if swallowed. Liquid and vapor cause severe burns. Harmful if inhaled.)

5.12 *Hydrochloric Acid, Standard Solution* (0.5 *N*)—Prepare and standardize a 0.5 *N* solution of HCl.

5.13 *Hydrochloric Acid* (10 %), a solution containing 10 % by weight of concentrated HCl in water, with a permissible variation of 0.5 %.

5.14 *Hydrochloric Acid* (1 + 3)—Mix one volume of concentrated HCl (37 %) with three volumes of water.

5.15 *Methyl Red Indicator Solution*. (**Warning**—Flammable. Avoid skin contact or ingestion.)

5.16 *Nitric Acid* (1 + 4)—Mix one volume of concentrated nitric acid (70 %) (**Warning**—Poison. Corrosive. Strong oxidizer. Contact with organic material may cause fire. May be harmful if swallowed. Liquid and vapor cause severe burns) with four volumes of water.

5.17 *Phenolphthalein Indicator Solution*—The phenolphthalein solution shall be prepared by dissolving 1.0 g phenolphthalein (**Warning**—In addition to other precautions,

<sup>12</sup> The sole source of supply of *n*-hexane, high-purity grade, known to the committee at this time is Phillips Petroleum Co., Special Products Div., Bartlesville, OK.

avoid skin contact or ingestion) in 50 mL of alcohol distilled as described in 5.4, adding 5 mL of water and neutralizing with NaOH or KOH.

5.18 *Potassium Hydrogen Sulfate* (KHSO<sub>4</sub>). (**Warning**—Poison. Harmful or fatal if swallowed. Causes severe eye and skin irritation or injury. Dust or mist may be harmful.)

5.19 *Potassium Hydroxide* (KOH), *Alcoholic* (0.5 N)—Prepare and standardize a 0.5 N solution of alcoholic potassium hydroxide. (**Warning**—Poison. Causes eye and skin damage.)

5.20 *Potassium Periodate* (KIO<sub>4</sub>). (**Warning**—May be irritating to skin and eyes. May react vigorously with reducing agents.)

5.21 *Sodium Carbonate*—(Na<sub>2</sub>CO<sub>3</sub>). (**Warning**—Harmful if swallowed. May cause skin irritation.)

5.22 *Sodium Hydroxide* (240 g/L)—Dissolve 240 g of sodium hydroxide (NaOH) (**Warning**—Poison. Causes eye and skin damage) in water and dilute to 1 L.

5.23 *Sodium Hydroxide Solution, Standard* (0.05 N)—Prepare and standardize a 0.05 N NaOH solution.

5.24 *Sulfuric Acid* (1 + 4)—Carefully mix one volume of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub> 95 %) with four volumes of water. (**Warning**—Poison. Corrosive. Strong oxidizer. Contact with organic material may cause fire. May be fatal if swallowed. Liquid and vapor cause severe burns. Harmful if inhaled. Contact with water liberates large amounts of heat.)

5.25 *Sulfuric Acid* (3 + 20)—Carefully mix 3 mL of concentrated sulfuric acid (95 %) with 20 mL of water.

5.26 *Toluene*. (**Warning**—Flammable. Vapor harmful.)

## 6. Sample

6.1 The sample size for the soap determination (Test Methods I and II for determination of insolubles, soap, fat, petroleum oil, and unsaponifiable matter) shall be from about 8 to 30 g, depending on the consistency of the grease, which is chiefly determined by the percentage of soap present. A 10 to 20-g sample is usually a convenient amount for No. 3 cup grease, while softer greases require a larger sample. The original sample shall be stirred or mixed until uniform.

6.2 Samples need not be weighed more closely than to 0.1 g.

## ASH DETERMINATION

### 7. General

7.1 The percentage of ash shall not be included in the total of the analysis.

NOTE 3—The determination of the total ash should not in general be regarded as of any great importance. It is, however, sometimes required. This determination is often unsatisfactory because of interaction between Na<sub>2</sub>CO<sub>3</sub> derived from the soap and inorganic insolubles. There is always likelihood of reaction with the porcelain crucible itself on account of the long continued heating necessary to burn off all carbon. Moreover, if much Na<sub>2</sub>CO<sub>3</sub> or K<sub>2</sub>CO<sub>3</sub> is present, the ash is fusible and often encloses carbon, making complete removal of the latter very difficult. Results will always be low in the presence of easily reducible oxides of volatile metals. There is also uncertainty as to when CaCO<sub>3</sub> has been completely ignited to CaO. Ash determinations made on the same sample in different laboratories are likely to vary widely.

### 8. Rapid Routine Test Method

8.1 Place a 2 to 5-g sample of the grease in a weighed porcelain crucible and weigh the sample to the nearest 0.1 g. If

lead or zinc soap is known to be absent, a platinum crucible is more convenient. Slowly burn off the combustible matter, and finally ignite the residue until the ash is free of carbonaceous matter. Cool the crucible and contents in a desiccator and weigh, reporting the result as percentage of ash.

### 9. Alternative Test Method

9.1 Burn the sample in accordance with 8.1 until the ash is nearly free from carbon. Cool the crucible and contents, dissolve the soluble portions in a little water, and add a slight excess of H<sub>2</sub>SO<sub>4</sub> (1 + 4), (**Warning**—Poison. Corrosive. Strong oxidizer. Contact with organic material may cause fire. May be fatal if swallowed. Liquid and vapor cause severe burns. Harmful if inhaled. Contact with water liberates large amounts of heat) running the acid in carefully from a pipet inserted under a small watch glass covering the crucible. Warm the crucible and contents on a steam bath until effervescence has ceased. Rinse the watch glass with water into the crucible. The solution, when tested with methyl red (**Warning**—Flammable. Avoid skin contact or ingestion) for free acidity, shall show free acid present. Evaporate the contents of the crucible to dryness and ignite the whole at a low red heat, adding a few small pieces of dry (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> (**Warning**—Harmful if swallowed) to drive off the excess SO<sub>3</sub>. After cooling and weighing, report the result as percentage of ash as sulfates.

NOTE 4—This test method gives more concordant results than the routine method (Section 8), but it requires more time and manipulation.

### 10. Qualitative Examination

10.1 An easily fusible ash, dissolving completely in water to give a strongly alkaline solution, indicates a grease containing sodium, potassium, or both. Lithium is indicated by a white infusible ash, readily soluble in water, giving a strongly alkaline solution. A white infusible ash, practically insoluble in water but imparting to it an alkaline reaction, may indicate calcium, with or without magnesium or aluminum. Zinc is shown by the yellow color of the ash while hot, and lead may be indicated by the presence of metallic globules or by the yellow color of the ash when cold.

10.2 Dissolve the ash in HNO<sub>3</sub> (1 + 4) (**Warning**—Poison. Corrosive. Strong oxidizer. Contact with organic material may cause fire. May be harmful if swallowed. Liquid and vapor cause severe burns) or HCl (1 + 3) (**Warning**—Poison. Corrosive. May be fatal if swallowed. Liquid and vapor cause severe burns. Harmful if inhaled.) Confirm the presence of the several bases by suitable chemical tests, following any standard scheme of qualitative analysis.

### 11. Quantitative Examination

11.1 For the quantitative examination of ash, use any standard analytical procedure, basing the choice of methods on the information gained from the qualitative tests. If only one base is present, a quantitative determination is, in general, unnecessary.

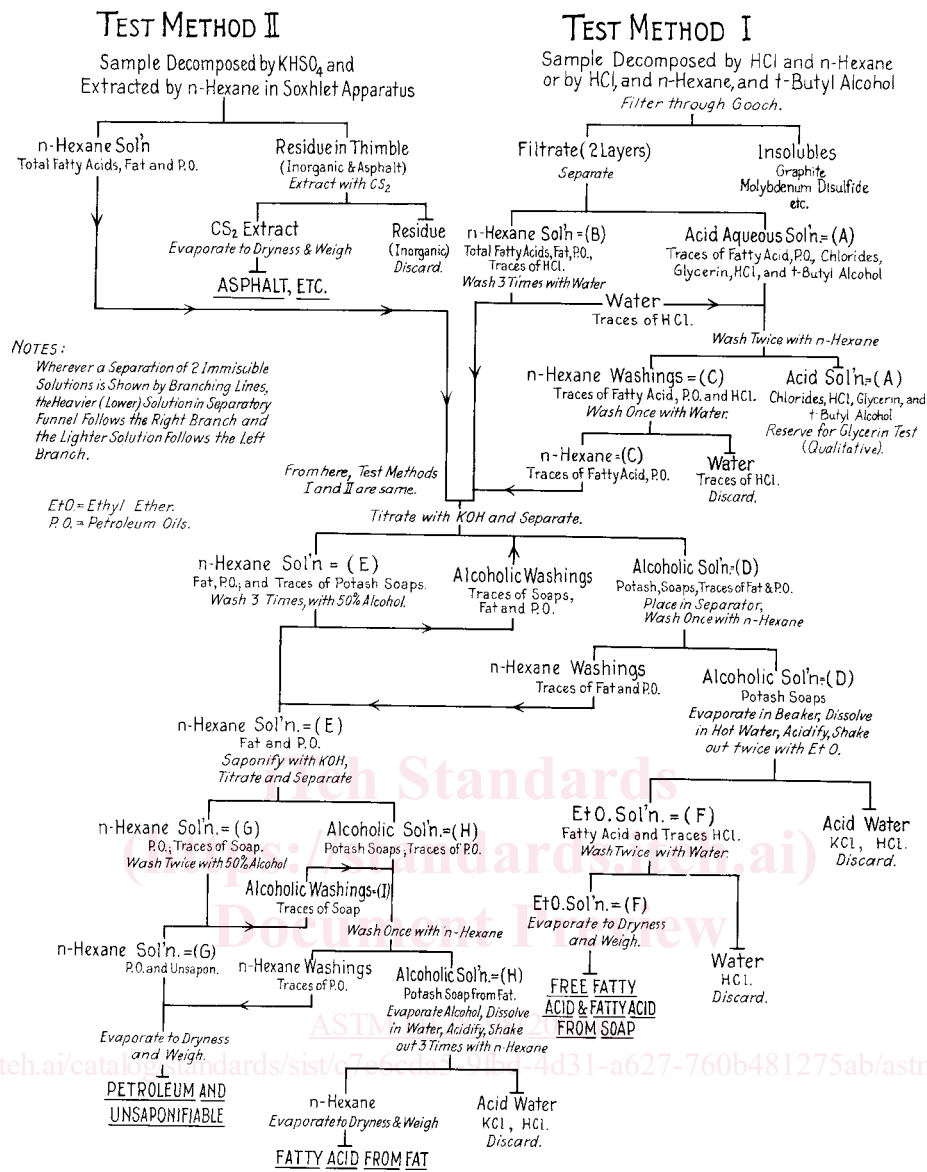


FIG. 1 Scheme of Grease Analysis

**INSOLUBLES, SOAP, FAT, PETROLEUM OIL, AND UNSAPONIFIABLE MATTER**

**12. Choice of Test Method**

12.1 Examine greases containing residuum, asphaltic oils and asphalt, tars, and so forth, using Test Method II, as these ingredients usually cause stubborn emulsions if a vigorous agitation process is applied at the start. Analyze all other greases using Test Method I. (See Fig. 1.)

*Test Method I*

**13. Insolubles**

13.1 If insolubles are present (see Note 5), weigh the sample (see section 6) in a small beaker, add 50 mL of HCl (10 %), and warm the beaker on a steam bath, stirring until all soap lumps have disappeared and the upper layer is clear. If undissolved mineral matter or other insoluble is present, filter both layers

while warm through a Gooch crucible provided with a suitable mat, wash the beaker and crucible with warm (60 to 63°C) water (see Note 6) and *n*-hexane, (**Warning**—Extremely flammable. Harmful if inhaled. May produce nerve cell damage. Vapors may cause flash fire.) Finally, wash the crucible with alcohol (**Warning**—Flammable. Denatured. Cannot be made nontoxic.) collecting the alcohol washings separately, and discarding them. Dry the crucible and contents at 120°C and weigh, reporting the result as percentage of insoluble matter (graphite, molybdenum disulfide, and so forth).

NOTE 5—If no insolubles are present, omit the procedure given in Section 13.

NOTE 6—Throughout the test method where the word warm is used, it is to be understood that a temperature of 60 to 63°C is to be used.

**14. Soap**

14.1 If insolubles are absent, decompose a sample of the grease, either by the two-phase procedure as described in 14.2

or by the single-phase procedure as described in 14.3. In either case, if the contents of the flask or beaker remain liquid, follow the procedure described in 14.4. If contents congeal, or if, in the case of the two-phase decomposition, solid particles form, follow the procedure described in 14.5.

14.2 Weigh the grease sample (see Section 6) into either a 250-mL or a 500-mL Erlenmeyer flask, spreading the sample over the lower inside surfaces of the flask. Add 20 mL of *n*-hexane followed by 50 mL of HCl (10 %) and several boiling chips. Digest the sample by boiling under a reflux condenser until it is completely decomposed. Formation of a clear oil layer is evidence of complete decomposition. A digestion time of 3 h is generally sufficient; however, more vigorous boiling or use of a stronger HCl solution or additional *n*-hexane will be found necessary for greases difficult to decompose. Allow the contents of the flask to cool to room temperature.

14.3 Weigh the grease sample (see Section 6) into a 250-mL beaker. Add a TFE-fluorocarbon-coated magnetic stirring bar, 50 mL of *t*-butyl alcohol (**Warning**—Flammable liquid; causes eye burns), 50 mL of *n*-hexane, 2 drops of butter yellow indicator (**Warning**—Flammable. Vapor harmful) and 2 mL of HCl (37 %). For heavy greases, 50 mL of toluene (**Warning**—Flammable. Vapor harmful) may be substituted for *n*-hexane. Note also that *t*-butyl alcohol will solidify if the temperature is approximately 24 to 27°C or below. Heat the beaker and contents on a magnetic stirring hot plate. Stir magnetically and break up large lumps with a glass rod, but avoid boiling the solution. If the indicator becomes yellow, add concentrated HCl (37 %) in 1-mL increments until the color remains red. Continue the heating and stirring until all grease has dissolved, which indicates complete decomposition. For most grease, 10 to 15 min are usually sufficient. Disregard any inorganic salts that may precipitate. Cool the contents of the beaker to room temperature.

14.4 Transfer the contents of the flask or beaker to a separatory funnel, using *n*-hexane and water as washing liquids. Allow this solution (or the combined filtrate and washings, except the alcohol washings, from the determination of insolubles, Section 13, transferred to a separator), to clear and draw the aqueous layer, *A*, which contains all the bases as well as glycerin, into another separator. Wash the *n*-hexane layer, *B*, three times with 25-mL portions of water to remove HCl, adding the washings to *A*. Wash the aqueous solution, *A*, twice with 20-mL portions of *n*-hexane, *C*, and then set Solution *A* aside for examination for glycerin (Section 16). Wash Solution *C* once with 15 mL of water, which may then be discarded, and add *C* to *B*. If Solutions *B* and *C* are comparatively light-colored, an approximate determination of free fatty acids and fatty acids from soap can now be made by titrating the solution in the separator with 0.5 *N* alcoholic KOH solution (**Warning**—Poison. Causes eye and skin damage) using phenolphthalein (**Warning**—In addition to other precautions, avoid skin contact or ingestion) as the indicator, and using 200 as the average neutralization value of the fatty acid (that is, 1.0 g of fatty acid requires 200 mg of absolute KOH for neutralization). If Solutions *B* and *C* are dark, add a few drops of

phenolphthalein solution and sufficient 0.5 *N* alcoholic KOH solution to make the alcoholic layer distinctly alkaline after vigorous shaking.

NOTE 7—Capital letters reference solutions given in Fig. 1.

14.5 Heat the contents of the flask or beaker to approximately 63°C and transfer to a separator that has been previously warmed by flushing with warm water, using warm *n*-hexane and warm water as washing liquids (**Warning**—see 14.5.1). Allow this solution to clear and draw the aqueous layer, *A*, which contains all the bases as well as glycerin, into another separator. Wash the *n*-hexane layer, *B*, three times with 25-mL portions of warm water to remove HCl, adding the washings to *A*. Wash the aqueous solution, *A*, twice with 20-mL portions of warm *n*-hexane, *C*, and then set Solution *A* aside for examination for glycerin (see Section 16). Wash Solution *C* once with 15 mL of warm water, which can then be discarded, and add *C* to *B*. If Solutions *B* and *C* are comparatively light-colored, an approximate determination of free fatty acids from soap can now be made by titrating the solution, which is at approximately 63°C, in the separator with 0.5 *N* alcoholic KOH solution using phenolphthalein as the indicator, and using 200 as the average neutralization value of the fatty acid (that is, 1.0 g of fatty acid requires 200 mg of absolute KOH for neutralization). If Solutions *B* and *C* are dark, add a few drops of phenolphthalein solution and sufficient 0.5 *N* alcoholic KOH solution to make the alcoholic layer distinctly alkaline after vigorous shaking.

14.5.1 (**Warning**—Extreme care should be exercised in handling warm *n*-hexane because of pressure developing in the stoppered separatory funnel. Invert the funnel and release pressure through the stopcock occasionally.)

14.6 If Solutions *B* and *C* from 14.4 and 14.5 have been titrated, add 0.5 to 1.0 mL excess of alkali before separating. The conservative addition of alcohol at this point can aid in securing rapid and sharp separation. Allow the two solutions to separate sharply and draw off the lower alcoholic layer, *D*, into another separator. Wash the upper *n*-hexane layer, *E*, three times, with 30, 25, and 20 mL of neutral 50 % alcohol, respectively, adding these washes to *D*. Wash Solution *D* with 25 mL of *n*-hexane, after which draw off *D* into a beaker and add the *n*-hexane to *E*. Evaporate Solution *D* to a small volume to remove alcohol, wash the residue of potassium soap into a separator with hot water, acidify with HCl, and shake out twice with 50 and 25 mL of ethyl ether, *F*, respectively. Run Solution *F* into another separator and wash twice with 20-mL portions of water, which can then be discarded. Transfer Solution *F* to a weighed beaker and evaporate to dryness on a steam bath, blowing with air to remove all traces of ethyl ether. (**Warning**—Extremely flammable. Harmful if inhaled. May cause eye injury. Effects may be delayed. May form explosive peroxides. Vapors may cause flash fire. Moderately toxic. Irritating to skin.) Heat the residue, consisting of free fatty acids and fatty acids from soap, for a short time on a steam bath, adding and evaporating 5-mL portions of acetone (**Warning**—Extremely flammable. Vapors may cause flash fires) until a constant weight is obtained and the last traces of water are removed. Determine the exact neutralization value on as large a sample of these fatty acids as possible.