OIL ANALYSIS

AUGUSTUS H. GILL

A SHORT HAND-BOOK
of
OIL ANALYSIS

BY

AUGUSTUS H. GILL, S.B., PH.D.
AUTHOR OF "GAS AND FUEL ANALYSIS FOR ENGINEERS," "ENGINE ROOM CHEMISTRY"
PROFESSOR OF TECHNICAL ANALYSIS AT THE MASSACHUSETTS
INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS.

REVISED TENTH EDITION

PHILADELPHIA AND LONDON
J. B. LIPPINCOTT COMPANY

Electrotyped and Printed by J. B. Lippincott Company
The Washington Square Press, Philadelphia, U.S.A.

PREFACE TO THE TENTH EDITION.

THE changes in this edition include, a section on the examination of Motor Gasoline, and a description of the latest model MacMichæl Absolute Viscosimeter, which in view of impending modifications are given in the Appendix. The special tests, methods of analysis, and the description of the special oils and greases have been revised where necessary, to bring the book thoroughly up-to-date.

Oil chemistry is expanding so rapidly, that the temptation is great to make the book more comprehensive. This would however increase its cost and defeat its original purpose—that of a *concise* manual *primarily* for *beginners.*

CAMBRIDGE, JANUARY, 1922

PREFACE TO THE FIRST EDITION.

THIS little book was written primarily to meet the needs of the author's own classes. It is given to the public in the belief that there is a demand for a concise manual for the analysis of oils, which shall give the methods of applying the usual physical and chemical tests to the mineral as well as to the animal and vegetable oils.

It is not designed to take the place of any of the existing books, but rather to serve as an introduction to them, more especially to Benedikt-Lewkowitsch, which is to the oil chemist what Fresenius is to the analytical chemist, and to which the writer wishes to express his own indebtedness. The writings of Schaedler, Redwood, Allen, and Brannt have also been freely consulted. Only the more commonly occurring oils are discussed, and these as regards their preparation, properties, analytical constants,—the highest, lowest, and average being given,—and finally their uses and adulterants.

In the use of this book it is assumed that the student is thoroughly familiar with the usual operations of volumetric and gravimetric analysis, and has attained some proficiency in organic chemistry.

Acknowledgments are due to Mrs. Ellen H. Richards for hints and suggestions, and to Mr. William L. Root for assistance in reading the proof.

BOSTON, November, 1897.

PRELIMINARY OBSERVATIONS.

SAMPLES of oil are almost always handled in the trade, and frequently brought for analysis, in a four-ounce "oil vial." The student will pour out a portion from the quart can, after thorough shaking, into such a vial. Before proceeding with the tests to be later described, it is well to make certain preliminary observations upon this sample.

The *turbidity,* showing the presence of water or of oils which imperfectly mix, and the *sediment,* either stearin or dirt, are to be noted; the *color* and *fluorescence,* or "bloom,"— the latter indicating the presence of mineral oils,—are next observed; the color varies from "water white," through straw, lemon-yellow, wine-red, or the oil may be opaque.

The *odor* and *taste* may reveal to experts much concerning the source of the oil under examination; for example, the fish oils, especially when warmed, have an unmistakable odor, and the presence of whale oil in sperm is often detected by its "nutty" taste.

By inverting the bottle when partially filled, and noting the way in which the oil runs off from the bottom and the number of drops, an approximate idea of the viscosity may be obtained.

CONTENTS.

PART I.

PHYSICAL AND CHEMICAL TESTS.

CHAPTER I.

PETROLEUM PRODUCTS.

(a) Burning Oils.

CHAPTER II.

PETROLEUM PRODUCTS.

(b) Lubricating Oils.

CHAPTER III.

ANIMAL AND VEGETABLE OILS.

CHAPTER IV.

GENERAL CONSIDERATIONS REGARDING LUBRICANTS.

PART II.

DERIVATION, DESCRIPTION, AND EXAMINATION OF CERTAIN OILS.

CHAPTER V.

PETROLEUM PRODUCTS.

A. OILS AND FATS. GLYCERIDES.

CHAPTER VI.

VEGETABLE OILS.

(1) Drying Oils.

(2) Semi-Drying Oils.

(3) Non-Drying Oils.

CHAPTER VII.

ANIMAL OILS.

(1) Marine Animal Oils.

(2) Terrestrial Animal Oils.

B. WAXES.

LIQUID WAXES.

CHAPTER VIII.

WASTE FATS. LUBRICATING GREASES. MISCELLANEOUS OILS. EDIBLE FATS. HARDENED OILS.

APPENDIX.

PART I.

PHYSICAL AND CHEMICAL TESTS.

PRELIMINARY OBSERVATIONS.

SAMPLES of oil are almost always handled in the trade, and frequently brought for analysis, in a four-ounce "oil vial." The student will pour out a portion from the quart can, after thorough shaking, into such a vial. Before proceeding with the tests to be later described, it is well to make certain preliminary observations upon this sample.

The *turbidity*, showing the presence of water or of oils which imperfectly mix, and the *sediment*, either stearin or dirt, are to be noted; the *color* and *fluorescence*, or "bloom"—the latter indicating the presence of mineral oils—are next observed; the color varies from "water white," through straw, lemon-yellow, wine-red, or the oil may be opaque.

The *odor* and *taste* may reveal to experts much concerning the source of the oil under examination; for example, the fish oils, especially when warmed, have an unmistakable odor, and the presence of whale oil in sperm is often detected by its "nutty" taste.

By inverting the bottle when partially filled, and noting the way in which the oil runs off from the bottom and the number of drops, an approximate idea of the viscosity may be obtained.

SAMPLING.

Oil sampling must be carefully done, as it is a difficult operation. This is due to the presence of "foots," "dirt," and water. These settle out on standing, and cannot usually be reincorporated with the oil.

In the case of tank cars, about six samples, at as many different levels, are withdrawn by means of a stoppered can on a pole. The stopper is so arranged that it can be withdrawn and replaced at different depths. The samples are mixed in proportion to the size of the layers; in case there be but two, samples are taken from each as it is drawn off: the volume of each layer is determined: about 50 pounds is so taken.

Samples from barrels can be taken after they have been well rolled about and also turned end over end, to ensure thorough mixing. This is usually done by an oil "thief"—a gigantic pipette, 30"x 1-½", with openings at the top and bottom of about ⅜ inch. It should not be inserted into the oil any faster than it rises in the tube. When solid the sample is taken by a tryer 2 inches across and 9-ft. long; samples are taken vertically and obliquely until 50 pounds are obtained.[1]

Samples are usually taken from one barrel or can, in twenty, or sometimes sixty: they are often taken at random. These different samples, as well as the oils, should be thoroughly mixed. Where samples are to be stored, glass containers, well filled, kept cool and in the dark, are preferable.

---

[1] J. Ind. & Eng. Chem. **11**, 1161 (1919).

A SHORT HAND-BOOK OF OIL ANALYSIS.

CHAPTER I.

PETROLEUM PRODUCTS.

(a) Burning Oils.

THE tests to be made are, in the order of their importance, flash test, fire test, specific gravity, distillation test, determination of sulphur, acidity, sulphuric acid test, test for mineral salts, determination of water.

Flash Test or Point.[1]—By flash point we understand the lowest temperature to which an oil must be heated to give off vapors which, when mixed with air, produce an explosive mixture. The results of this test will vary according to the quantity of air over the surface of the oil, and whether this be moving or still; also according to the distance of the testing flame from the surface of the oil. Furthermore, the size of the flame, the length of its time of action, its form and dimensions, and, lastly,

---

[1] The flash point is oftentimes a valuable means of detecting the admixture of substances; for example, 0.1 per cent. ether in alcohol may be discovered by this test. See Table II.

the manner of heating of the oil, will all influence the result.[1]

From the above statement and that of Dudley[2] the following points are to be especially noted:

1. *The Rate of Heating.*—The faster the oil is heated the lower will be the flash point, as more vapor is driven out.

2. *Size and Depth of Cup.*—From a large and shallow cup the liquid evaporates faster; hence the lower will be the flash point. The most constant results are obtained from a deep cup about half filled.

3. *Quantity of Oil.*—The larger the amount of oil the more vapor will be driven out; hence the lower will be the flash point.

4. *Distance of Testing Flame.*—The nearer or—what amounts to the same thing—the larger the testing flame the lower will be the flash point. A large flame may produce local superheating.

5. *Point of Application of Testing Flame.*—The flame should be applied at the edge, as the mixture of air and vapor is more complete; this is best effected by drawing the flame diametrically across the top of the cup. Dr. Dudley cites an instance in which the flash point obtained was considerably too high, owing to the fact that the testing flame was first applied in the centre of the cup.

6. *The thermometers* used should be frequently compared with a standard instrument.

7. *Draughts* should be carefully avoided.

---

[1] Engler and Haase, Z. anal. Chem., **20**, 3 (1881).

[2] American Engineer and Railroad Journal, **64**, 180 (1890).

Numbers 1 to 4 may be briefly summarized as follows: any cause producing the rapid evolution of a large amount of petroleum vapor tends to lower the flash point.

Barometric changes are, for practical work, negligible, each five millimeters between seven hundred and forty-five and seven hundred and seventy-five millimeters causes a variation of but 0.1° C.

Lenz[1] states that the initial temperature of the oil is of importance, and as a result of several hundred determinations recommends cooling the oil contained in the flashing cup to 0° C. before making the test. In case the oil contains water, it must be removed by treatment with calcium chloride or sulphate.

The apparatus in use in this country are divided into two classes,—covered testers, in which the cup is covered with a perforated metal or glass plate, and open testers, in which the cup is not so covered. In the author's opinion the covered testers are the more scientific and give the more concordant results, and should be made the standard instruments.

Covered Testers.—One of the best forms of testing apparatus is that devised by the Michigan State Board of Health in 1873, modified by Dr. A. H. Elliott, and now known as the "New York State Board of Health Tester," shown in Fig. 1.

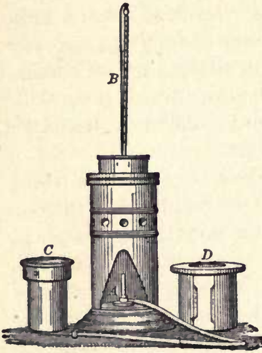
Description.—It consists of a copper oil cup, *D*, holding about ten ounces, the quantity usually

---

[1] Z. anal. Chem., **25**, 265 (1886).

contained in lamps, heated in a water-bath by a small Bunsen flame. The cup is provided with a glass cover, *C*, carrying a thermometer, *B*, and a hole for the insertion of the testing flame,—a small gas flame one-quarter of an inch in length.

FIG. 1.



New York State Board of Health tester.

Manipulation. — After describing the apparatus minutely, the regulations of the New York State Board of Health say,[1] "(2) The test shall be applied according to the following directions:

"Remove the oil cup and fill the water-bath with cold water up to the mark on the inside. Replace the oil cup and pour in enough oil to fill it to within one-eighth of an inch of the flange joining the cup and the vapor-chamber above. Care must be taken that the oil does not flow over the flange. Remove all air-bubbles with a piece of dry paper. Place the glass cover on the oil cup, and so adjust the thermometer that its bulb shall be just covered by the oil.

"If an alcohol lamp be employed for heating the

---

[1] Report of the New York State Board of Health, 1882, p. 495.

water-bath, the wick should be carefully trimmed and adjusted to a small flame. A small Bunsen burner may be used in place of the lamp. The rate of heating should be about two degrees per minute, and in no case exceed three degrees.

"As a flash torch, a small gas jet one-quarter of an inch in length should be employed. When gas is not at hand employ a piece of waxed linen twine. The flame in this case, however, should be small.

"When the temperature of the oil has reached 85° F. the testings should commence. To this end insert the torch into the opening in the cover, passing it in at such an angle as to well clear the cover, and to a distance about half-way between the oil and the cover. The motion should be steady and uniform, rapid and without any pause. This should be repeated at every two degrees' rise of the thermometer until the thermometer has reached 95°, when the lamp should be removed and the testings should be made for each degree of temperature until 100° is reached. After this the lamp may be replaced if necessary and the testings continued for each two degrees.

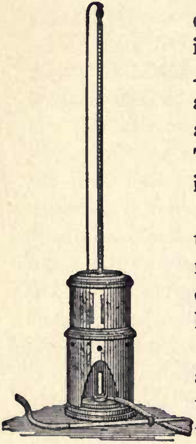
"The appearance of a slight bluish flame which passes over the entire surface shows that the flashing point has been reached.

"In every case note the temperature of the oil before introducing the torch. The flame of the torch must not come in contact with the oil.

"The water-bath should be filled with cold water for each separate test, and the oil from a previous test carefully wiped from the oil cup."

Open Testers.—The Massachusetts statute is by no means as definite as that of New York; the courts have decided that custom fixes the method of testing. The law says,[1] "No person shall offer for sale. . . illuminating oils made from coal or petroleum which will evaporate a gas under 100° F. [that is, the flashing point is 100° F.—A. H. G.], or ignite at a temperature of less than 110° F., to be ascertained by the application of Tagliabue's or some other approved instrument."

FIG. 2.



Tagliabue's open tester.

Manipulation.—Tagliabue's open tester (Fig. 2) is the official instrument. This is similar to the preceding, except that it is smaller, has a glass oil cup and no cover.

The water-bath is filled as before, and the oil cup to within three-thirty-seconds of an inch of the top. The heating flame is adjusted so that it is three-fourths of an inch high, and the heating proceeded with at the rate of two and a half degrees per minute, until 97° F. is reached, when the test flame is applied and the testings made every three degrees until the flash point is reached, shown by a blue flame passing over the entire surface. The whole time of making the test should be half an hour.

---

[1] Revised Statutes of Massachusetts, 1902.

Fire Test.—The fire test of an oil is the lowest temperature at which it will give off vapors which when ignited will burn *continuously.* It is made by continuing to heat the oil (the cover being removed in the case of a closed tester without slipping out the thermometer) at the same rate after the flash test is made and noting the point as indicated above. The flame is extinguished by a piece of asbestos board and the heating discontinued. In the case of many illuminating oils this point is from 10° to 20° F. higher than the flash point.

Notes.—In the case of "Mineral Sperm" (300° F. fire test petroleum) these tests should be made with the instrument for lubricating oils (page 39). The heating should be at the rate of 15° F. per minute, and the testing flame first applied at 230° F., and then every seven degrees until the flashing point is reached.

The most satisfactory way of making these tests is to place the watch upon the desk and read the thermometer at the expiration of every minute, noting each reading down in the proper column in the laboratory note-book.

Specific Gravity.—This is usually effected by the hydrometer; a hydrometer jar is four-fifths filled with the oil, a Baumé hydrometer introduced into it, and the depth read off to which the instrument sinks in the oil. This may be effected by placing a strip of white paper back of the jar and noting the point at which the lower meniscus of the oil touches the scale. The temperature of the oil is taken at the same time, and in case it be not 60° F. (15.5° C.), for every increase of 10° F. (5.5° C.) subtract 1° Baumé from hydrometer reading. The specific gravity may be found by the formula $\frac{140}{130+B^{\circ}}$, representing the reading Baumé at 15.5° C.[1]

Notes.—Inaccurate graduation may cause an error of 0.001, but if the instrument be carefully calibrated it is accurate to 0.0002.[2] The student will make this test upon the oil at the ordinary temperature and correct the gravity for temperature as given above. In practice this can be done by Tagliabue's "Manual for Inspectors of Coal Oil," which gives the readings at 60° F. for any gravity from 20° to 100° Baumé, between 20° F. and 109° F.

Distillation Test.—As a means of evaluating samples of kerosene, Beilstein[3] recommends the fractional distillation of two hundred cubic centimeters, using a tower. As the method of Engler is more frequently employed, that will be described.

He uses a peculiar boiling flask, six and five-tenths centimeters in diameter, with neck fifteen centimeters long, and with the side tube about nine centimeters from the springing of the bulb; this is connected with a Liebig condenser and heated by a small lamp with a shield.

Manipulation.—One hundred cubic centimeters of the oil are measured into the boiling flask and distilled at the rate of two to two and five-tenths

---

[1] U. S. Bureau of Standards Circular No. 57. "U. S. Standard Tables for Petroleum Oils."

[2] Wright, J. Soc. Chem. Ind., 11, 302 (1892).

[3] Z. anal. Chem., 22, 309 (1883).

cubic centimeters per minute, the distillate being caught in a 25 cc. burette or graduate. When the distillation is to be broken, the lamp should be taken away and the temperature allowed to sink twenty degrees and again brought to the breaking or fractionating point, as long as any considerable quantity goes over. The distillation is first broken at 150° C., and then each fifty degrees until 290° C. is reached; in this way a much better idea of the value of the oil is obtained than if the distillation were allowed to proceed continuously between these points. The lighter portions, for example, those between 150° and 200°, burn much better than those between 250° and 290°; the heavy portions of American petroleum burn much better than those of the Russian oils.

The averages from four samples of Caucasian and ten samples of American oils subjected to this test were as follows, in per cent. by volume:[1]

	Below 150° C.	150° –290° C.	Above 290° C.
Caucasian petroleum..........	8.0	86.6	5.4
American petroleum...........	16.9	57.1	26.0

For evaluating samples of *motor gasoline*,[2] the distillation is similarly made, the first break being made at 105°, the second at 140° and the third at 190°. The fraction below 105° gives an idea of the ease with which a motor using it could be started in cold weather. The residue in the flask shows the extent to which a very heavy naphtha or kerosene has been mixed with the gasoline. The heavier gasoline has the greater heating value per gallon.

---

[1] Veith, "Das Erdoel," p. 244.

[2] See Appendix, p. 210, et seq.

Determination of Sulphur.—In addition to the preceding tests, Professor Peckham[1] considers the determination of sulphur to be of considerable importance. The deleterious effect of the oxides of sulphur upon hangings and bindings is well known, sulphuric acid being their ultimate product. The sulphur exists in combination, partly as compounds formed from the sulphuric acid used in refining[2] and partly as sulphides already formed in the oil. Its qualitative detection may be effected by heating the oil to its boiling point with a bright piece of sodium or potassium. If sulphur compounds be present, a yellowish layer is formed upon the metal. After cooling add distilled water drop by drop until the metal is dissolved, and test for sulphides with sodium nitro-prusside.

For the quantitative determination of sulphur many methods have been proposed. Engler[3] and Kissling[4] burn the oil in an apparatus similar to that used for the determination of sulphur in illuminating gas. This can be easily made from a small test-tube three-eighths of an inch in diameter and two and three-eighths inches long, fitted with a stopper carrying a narrow piece of tubing through which passes a piece of lamp-wicking[5]—the whole serving as a small lamp. This is burned under a funnel with the stem bent to connect with two wash-

---

[1] Report upon Petroleum.

[2] Vohl, Dingler's pol. J., 216, 47 (1875).

[3] Chem. Ztg., **20**, 197; abstr. J. Soc. Chem. Ind. **15**, 383 (1896).

[4] Ibid., 199; abstr. Analyst, 21, 162 (1896).

[5] Conradson, J. Ind. and Eng. Ch., 2, 171 (1910), has found as much as 40 per cent. of the sulphur in this wick.

bottles containing bromine water and the products of the combustion of the oil sucked through these.

The lamp is partly filled with the oil to be tested and weighed, burned until about a gram of oil has been consumed and again weighed. The sulphuric acid formed in the bottles containing bromine water is determined in the usual way with barium chloride. The determination should of course be made in an atmosphere free from sulphur. Allen and Robertson[1] find the foregoing process inapplicable to gasolines and to heavy residues. For all oils and combustibles, they find the combustion in a calorimetric bomb with oxygen at 30–40 atmospheres pressure, to be accurate, rapid and dependable. The sulphuric acid can be estimated as barium sulphate by the nephelemeter.[2] The method of Barlow[3] by combustion in a stream of oxygen and subsequent absorption of the products in sodium-carbonate is also accurate but tedious, and requires constant attention. The percentage of sulphur should not exceed 0.05; Engler, *l.c.*, and Kissling[4] found 0.02 to 0.03 in the Pennsylvania, and 0.04 to 0.05 in the Lima kerosenes.

Detection of Acidity.—Shake equal quantities of oil and warm water in a test-tube, pour off the oil, and test the water with litmus paper. If the water be strongly acid, the quantity may be determined as in "Free Acid," page 82.

---

[1] Eighth Inter. Cong. App. Chem., **10**, 25. Chem. Abstr. **6**, 2997 (1912).

[2] Muer, J. Ind. & Eng. Chem., **3**, 553 (1911).

[3] J. Am. Chem. Soc., **26**, 341 (1904).

[4] Ch. Rev. d. F. & H. Ind., **14**, 157 (1906), Anal., **31**, 342.

The acid in this case is most probably sulphuric, coming from the refining process.

Sulphuric Acid Test.—The object of this test is to judge of the degree of refinement of the oil, a perfectly refined oil giving little or no color when submitted to the process. One hundred grams of oil and forty grams of sulphuric acid, 1.73 specific gravity, are shaken together for two minutes in a glass-stoppered bottle and the color of the acid noticed. In accurate work this color is matched by solutions of Bismarck brown.[1]

Mineral Salts.—Salts of calcium or magnesium when dissolved in the oil diminish its illuminating power; their action is to form a crust on the wick and prevent access of air.

Redwood[2] states that 0.02 gram of either of these salts in one thousand grams of oil diminishes the illuminating power thirty to forty per cent. in eight hours.

They are determined by distilling one hundred or two hundred cubic centimeters of the oil down to about twenty cubic centimeters, evaporating and igniting this residue, and subsequently treating with hydrochloric acid. The calcium and magnesium are then determined in the usual way.

Determination of Water.[3]—By rubbing the oil together with a little eosin on a glass plate the oil will take on a pink color if water be present. Allen[4]

---

[1] J. Soc. Chem. Ind., **15**, 678 (1896).

[2] Dingler pol. J., **255**, 427 (1887).

[3] See, also, Davis, J. Am. Chem. Soc., **23**, 487 (1901). Allen & Jacobs, Bureau of Mines Technical Paper 28.

[4] Commercial Organic Analysis, ii. 491.

states that water in oils may be determined by the addition of a weighed amount of gently ignited plaster of Paris. This is washed with a little gasoline, dried at a gentle heat, and reweighed, the gain in weight being the water present.

Another method of determination consists in distilling off the water in a suitable apparatus and measuring it after the method of Dean for the determination of moisture in creosoted wood.[1]

Charitschkow[2] determines water in naphtha by mixing with an equal volume of benzole, whirling in centrifugal machine and measuring the water.

It is to be noted that one per cent. of water in an oil extinguishes the flame when making the flash test: three or four per cent. are apparently without influence on the viscosity.[3]

REFERENCES.

In addition to the literature previously given, the student is referred to the following:

ELLIOTT, A. H., New York State Board of Health Report, 1882, pp. 449–496. This gives comparative tests of the various testers and a résumé of bibliography and patents up to that year.

PECKHAM, S. F., "Report on the Production, Technology, and Uses of Petroleum and its Products," U. S. Census Report, 1885.

THÖRNER, W., Chemiker Ztg., 10, 528, 553, 573, 582, 601; abstracted in J. Soc. Chem. Ind., 5, 371 (1886). "Petroleum as an Illuminating Agent."

NEWBURY and CUTTER, Am. Chem. J., 10, 356 (1888). "On the Safety of Commercial Kerosene Oil."

AISINMAN, Chem. technische Vorträge, ii. 325. German methods of testing.

BRADLEY & HALE "Explosions of Kerosene," J. Ind. and Eng. Chem., 1, 344 (1909).

U. S. Fuel Administration Committee on Standardization of Petroleum Specifications Bulletins, 1 and 2, 1919.

---

[1] J. Ind. & Eng. Chem. **12**, 486 (1920).

[2] Charitschkow, Chem. Ztg., **30**, 93 (1906).

[3] Charitschkow, Chem. Ztg., **31**, 376 (1908).

CHAPTER II.

PETROLEUM PRODUCTS.

(b) Lubricating Oils.

THE tests to be made are, in the order of their importance, viscosity, specific gravity, evaporation, cold test, flash test, fire test, test for soap, heating test, demulsibility test, test for antifluorescents, friction test.

The office of a lubricant is to prevent the attrition of axle and journal by interposing itself between them in a thin layer, upon which the shaft revolves. The ideal lubricant is that which has the greatest adhesion to surfaces and the least cohesion among its own particles, or, as the practical man expresses it, the most fluid oil that will do the work and stay in place. The determination of its viscosity or "body" is then of the first importance.

Viscosity is the degree of fluidity of an oil or its internal friction. It is independent of the specific gravity of the oil, although this in the pipette instruments influences the time of efflux. Within certain limits it may be taken as a measure of the value of oil as a lubricant, by comparing the viscosity of the oil under examination with that of other oils which have been found to yield good results in practice.

The instruments employed for its determination may be divided into two classes,—pipette viscosimeters, giving time of efflux, as those of Engler, Saybolt, etc., and torsion viscosimeters, giving retardation due to oil, those of Napier, MacMichæl, Doolittle.

In expressing viscosity, consequently, it is necessary to give the name of the instrument with which it is determined. It is sometimes expressed as specific viscosity, that is, the time of the oil divided by the time of water: this is only comparative when done with instruments of the same name, that is, specific viscosity Engler is not the same figure as specific viscosity Saybolt. Besides this manner of stating viscosity, it is occasionally expressed in absolute (c. g. s.) units, dynes or poises.[1] This is possible when the diameter of the orifice, its length, the quantity and specific gravity of the oil, its time of efflux and change of head are known. Where it is impracticable to determine all these data, by direct measurements, the readings of a viscosimeter may be changed into dynes by determining the viscosity in seconds of standard solutions of glycerine, the viscosity of these being found in dynes or poises from Table XVII. Or it may be done by use of the plots in the appendix.

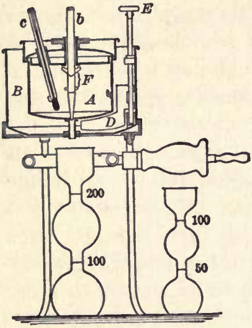
Engler Apparatus.—*Description.*—The apparatus (Fig. 3) consists of a flat, brass cylindrical vessel, *A*, 106 mm. in diameter and about 62 mm. deep, holding 240 cc., provided with a jet 2.9 mm. in diameter and 20 mm. long. This vessel is gilt inside and the jet, in the standard instruments, is of platinum—ordinarily it is made of brass; the vessel is surrounded with

---

[1] McIlhiney, J. Ind. and Eng. Chem., *8*, 433 (1916) Deeley & Parr, Phil. Mag. [6] *26*, 87 (1913).

a bath, *B*, either of water or oil, provided with a stirrer and heated by a ring burner. The jet is closed by the wooden valve, *F*, passing through the cover, and a thermometer, *c*, shows the temperature of the oil; three studs show the height to which *A* is filled and at the same time when it is level. The oil ordinarily is discharged into the 200 cc. flask, although in case the oil or time be limited, 100 or 50 cc. may be used and the time of efflux multiplied by a suitable factor. The instrument is standardized with water, 200 cc. of which at 20° C. should run out in from 50 to 52 seconds.

FIG. 3.



Engler apparatus.

Manipulation.—The instrument is thoroughly cleaned with alcohol and ether if necessary and dried; any suspended matter is removed from the oil, which is poured into it up to the level of the studs, stirred until 20° C. is reached and the bath adjusted to the same temperature. The flask is placed beneath the orifice, the plug raised and the time required for 200 cc. of oil to flow out is noted; this is divided by the water value of the instrument and gives the relative or specific viscosity. If only 50 cc. are allowed to run out the time must be multiplied by 5., and if 100 cc., by 2.35. If only 50 cc.

were put in and 40 cc. allowed to run out multiply this time by 3.62 to obtain the time for 200 cc.; if 60 cc. and 50 cc. run out multiply by 2.79[1]. If it be desired to express the viscosity in absolute measure (c.g.s. units) it can be done by reference to Table IX. It should be noted that specific viscosity obtained with a different type of instrument, *e.g.*, the Saybolt, is not the same as with the Engler.

The Saybolt Viscosimeter.[2]—The Standard Universal Viscosimeter is the one now used for testing Cylinder, Valve, and similar oils at 210° F.; Reduced Black Oils at 130° F.; Spindle, Paraffine, Red, and other distilled oils at 100°F.

The Universal Viscosimeter. — *Description.* — This consists of a brass tube, *A*, forming the body of the pipette provided with a jet, *K*. The upper part of the pipette is surrounded with a gallery, *B*, which enables a workman to fill it to the same point every time. The pipette is contained in a water-bath, *C*, which can either be heated by steam or a ring burner, *D;* a tin cup with spout, a strainer, thermometer, pipette with rubber bulb, stop watch, and beaker for waste oil complete the outfit. It may be used for testing Cylinder, Valve, and similar oils with bath at 212° and oil at 210°; for testing Reduced, Black Oils,

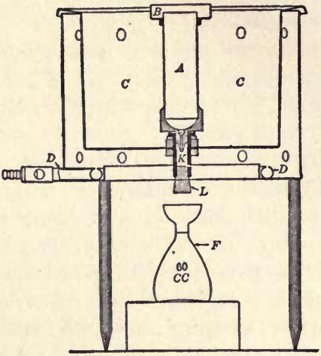
---

[1] Gans, Chem. Revue der Fett & Harz, Ind., **6**, 221 (1899.)

[2] Redwood, J. Soc. Chem. Ind, **5**, 124 (1886). This was formerly made in three forms, A, B, C. Apparatus "A" was the standard for testing at 70° F. Atlantic Red, Paraffine, and other distilled oils; "B" for testing at 70° F. Black Oils of 0°, 15°, 25°, and 30°, Cold Test, and other reduced oils up to, but not including, Summer Cold Test Oil. Apparatus "C" was used for testing at 212° F. Reduced, Summer, Cylinder, Filtered Cylinder, XXX Valve, 26.5° Bé., and other heavy oils

bath and oil at 130°; for testing Spindle, Paraffine, Red and other distilled oils, bath and oil at 100°. When used for testing at 212° F., it may be used with either gas or steam alone or both in combination. If with both, the steam may be introduced slowly, more for its condensation to replace evaporation than for real heating purposes, depending upon the gas flame to reach the boiling point, and keeping it there during the operation of test. The bath vessel should always be kept full during a test, whether at 212°, 130°, or 100°. When used at 130° or 100°, gas alone is used to bring the bath to the prescribed temperature, and turned off during the operation of test, the large size of the bath usually permitting making one test without reheating.

FIG. 4.



Universal viscosimeter.

Its dimensions are as follows:[1]

	Min. mm.	Normal mm.	Max. mm.
Outer diameter of outlet tube at lower end	2.8	3.0	3.2
Average head calculated	71.6	73.6	75.6
Diameter of pipette A	29.55	29.75	29.95
Height of overflow rim above bottom of outlet tube	124.0	125.0	126.0
Length of outlet tube	12.15	12.25	12.35
Diameter of outlet tube	1.75	1.765	1.78
Capacity of pipette A	70 cc.		

Manipulation.

1. Have the bath of water prepared at the prescribed temperature.

2. Have the oil strained into one of the tin cups, in which cup it may be heated up to about the standard temperature.

3. Clean out the tube with some of the oil to be tested by using the plunger sent with the instrument.

4. Place the cork (as little distance as possible) into the lower outlet coupling tube just enough to make air-tight, but not far enough to nearly touch the small outlet jet of the tube proper (one-eighth to one-quarter of an inch may be enough).

5. Pour the oil from the tin cup (again through the strainer) into the tube proper until it overflows into the overflow cup up to and above the upper edge of tube proper.

6. Now again see that the bath is at the prescribed temperature.

7. Use the thermometer sent with the instrument by stirring to bring the oil just to the standard temperature.

8. Remove the thermometer.

---

[1] A.S.T.M.Tech. Papers, 18, 364 (1918).
U. S. Bureau Standard Tech. Papers, 100 & 112.

9. Draw from the overflow cup, with a pipette, all the surplus oil down to and below the upper edge of tube proper. This insures a positive starting head.

10. Place the 60 cc. flask under and directly in line with the outlet jet, and as close to the coupling tube as is practical to permit of room for drawing the cork.

11. With the watch in left hand draw the cork with the right, and simultaneously start the watch.

12. The time required in the delivery of 60 cc. is the viscosity.

13. Clean out the tube proper before each test with some of the oil to be tested.

14. No drill or other instrument should ever be used in the small outlet jet of tube proper.

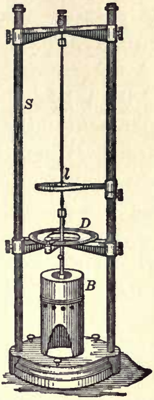
Notes.—Instead of timing the oil as given in the directions above, the writer has found it better to start the watch, and the instant the second-hand crosses the sixty seconds mark *twist* out the cork with the right hand.

The tube should be cleaned out before each test with some of the oil to be tested. Black oils or any oil containing sediment should be carefully strained before testing or "running," as it is technically termed. The instruments should be carefully guarded from dust when not in use.

The results obtained with this instrument are not the same in many cases as those furnished by the A, B, and C instruments, but they seem to have been adopted by the trade generally. Tables V–IX, XVI and XVII of the appendix will give a means of comparing the results obtained with the Saybolt, Doolittle, and Engler Viscosimeters.[1]

It is worth noting that three or four per cent. of water are apparently without influence on the viscosity.

FIG. 5.



Doolittle's torsion viscosimeter.

Doolittle's Torsion Viscosimeter.[2]—*Description.*—The apparatus consists of a cylinder (Fig. 5) rotating in the oil, and a graduated disk, *D*, to measure the amplitude of rotation. These are supported by a fine piano wire from the substantial stand *S*, provided with levelling screws; a lens, *l*, enables the graduations on the disk to be read more accurately, and a bath, *B*, filled with water or oil serves to maintain any desired temperature. The instrument should be so adjusted that it will read within one-half degree of the zero point on either side of it when vibrating through an arc of one hundred and eighty degrees; this can be effected by loosening the set screw at the top and turning the pin which holds the wire.

Manipulation.—Immerse the friction cylinder in the oil by slipping its stem into the stem of the disk, and adjust the temperature very carefully to

---

[1] Also Waidner, Proc. Am. Soc. Test. Mat. **15**, I, 284 (1915) and Meissner, Rev. d. Fett & Harz Ind. **19**, 30 (1912).

[2] Doolittle, J. Am. Chem. Soc., **15**, 173, 454 (1893).

the point at which it is desired to determine the viscosity; great care must be taken to keep this temperature constant during the test. Either a water-bath or bath of lard oil—according to the temperature desired—may be used. The oil in the cup should cover the cylinder with a layer three-sixteenths of an inch deep when it is swinging freely, and it should be in the centre of the cup.

By lifting the milled head at the top of the instrument out of the notch, and turning it completely around from right to left until it drops into the notch again, the wire is rotated three hundred and sixty degrees. By raising the disk by means of the cam the friction cylinder will rotate in the oil by virtue of the torsion of the wire. The disk will rotate three hundred and sixty degrees and a portion of another arc, which latter is the first reading, —the end of the first swing = 355.6° right. The left-hand swing is ignored, and the arc on the next swing to the right = 338.2° right, is read. The retardation produced by the oil is 355.6°—338.2° = 17.4°. The vibrations should now be stopped, and the head should be turned in the opposite direction and the readings to the left taken, and the average of the two considered as the retardation of the oil.

The results are expressed in the number ol grams of sugar contained in one hundred cubic centimeters of sugar syrup at 60° F., its viscosity being taken at a temperature of 80° F. In the example cited, 17.4° (with the small cylinder) represents a viscosity of 65.6; this means that if 65.6 grams of granulated sugar were dissolved in water at 60° F., made up to one hundred cubic centimeters and then heated to 80° F., its viscosity would be the same as that of the oil under examination.

The readings of the first and second swings are to be taken, as later vibrations give different results. The wire and cylinder should be handled with great care, as they are very sensitive to abuse. The wire should be greased with tallow occasionally, and in case of a new instrument, restandardized after six months' use. In case a new wire is inserted the instrument must be recalibrated. When not in use, the 0° point should be kept under the index, the disk upon its supports, and the wire without torsion.

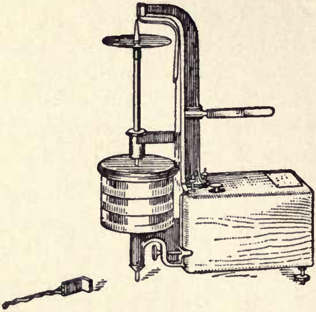
MacMichæl's Viscosimeter[1].—This is an instrument of the torsion type (Fig. 6) in which a disk is suspended in a cup of fluid, the latter being rotated, and the torsion it produces on the disk noted. The disk is suspended by a gold-plated, steel wire 10 inches long, held between two grooved pins at the top of the standard. The brass cup is oil jacketed, the oil covering the wires ½ inch and heated electrically, or it may be cooled by ice or brine. A bent thermometer passing through the cover indicates the temperature, which may be controlled easily within a fraction of a degree. The graduated dial at the top of the disk is rotary and may be easily set to 0°. A dash pot filled

---

[1] J. Ind. & Eng. Chem., 7, 961 (1915). id. 12, 282 (1920). Appendix p. 209.

with engine oil on the stem of the disk damps the action of the motor. In operating, the instrument is levelled, the cup is filled to the mark with the fluid to be tested (about 100 cc.), the temperature adjusted, the cup rotated and the readings of the dial noted. These are in degrees of angular deflection, 300 to the circumference, and noted as °M. = $\frac{1}{1000}$ poise.[1] Water at 20° should read 10° M.[2] The smallest, or "practical unit" is 1° M.: by changing the decimal point, practical units, absolute units or specific viscosity may be obtained at one reading of the dial, no calculations being required. Three strengths of wire are supplied, giving water readings of 1°, 10° and 100°, covering ranges of viscosity to 5000° M. or 5 poise.

Fig. 6.



MacMichael's Viscosimeter.

The instrument should be calibrated by solu-

---

[1] A poise is a dyne per cm^2.

[2] Or 1 centipoise.

tions of pure glycerine, the absolute viscosity of which is known (Table XVII): the purity of the glycerine can be determined by a specific gravity determination,[1] there being nothing else but water present, or by standard solutions of cane sugar. (Table XVIII, p. 198.) The accuracy of the instrument is well within 0.5 per cent. The instrument is very rapid, the time required for a reading being very short. It can be applied to colloidal or lumpy solutions or suspensions, as limes, clay, glues, gums, explosives, paints or catsups.

Specific Gravity.—1. *By the Hydrometer* (p. 17).

2. *By the Westphal Balance.*—This is a specially constructed instrument, with a glass plummet carrying a thermometer counterbalanced by a weight. Upon immersing the plummet in a liquid, the positions of weights, which must be added to restore the equilibrium, represent the specific gravity directly. The largest weight represents the first decimal place, the next the second, and so on. The instrument is placed upon a level table, and by means of the levelling screw is brought into adjustment,—*i.e.*, so that the point upon the beam is exactly opposite the point upon the fixed part.

The plummet is now placed in the vial or balance jar containing the oil, cooled to 15.5°[2] C., hung upon the balance, being careful to completely immerse it in the oil, weights added to restore the

---

[1] "Lubrication and Lubricants," Archbutt and Deeley, pp.132-143.

[2] A correction of 0.000626 can be made for each variation of 1° C.

equilibrium, and the specific gravity read off as above described.

Notes.—In using the instrument care should be taken to place the riders at right angles to the beam, otherwise an error of 0.0005 may be introduced; furthermore, the loop upon the knife-edge should always be in the same position. In buying an instrument the spaces upon the beam should be tested with dividers to insure their equality, otherwise serious errors may be caused.[1] The limit of accuracy is about 0.0005.[2]

Care should also be taken that the plummet does not touch the sides of the jar or vial.

For solid fats and some oils the specific gravity is taken at 100° C., using a special plummet.

McGill[3] states that the balance is more sensitive for viscous oils when the specific gravity of the plummet is 4.0 than when it is 2.0.

Evaporation Test.[4]—The object of this test is to determine what percentage of an oil—more especially a spindle oil—is volatile when exposed to nearly the same conditions as it is on a bearing.

The oil is exposed upon annular disks of filter-paper one and five-eighths inches outside diameter, with hole five-eighths of an inch in diameter, which have been standing in a sulphuric acid desiccator for several days, contained in a flat watch-glass.

---

[1] Allen, Analyst, 14, 11; Stock, ibid., 50 (1889).

[2] Richmond, ibid., 65. [3] Analyst, 21, 156 (1896).

[4] See, also, Archbutt, J. Soc. Chem. Ind., 15, 326 (1896), and Waters J. Eng. and Ind. Chem. *5*, 394 (1913).

Manipulation.—The watch-glass and paper are weighed—to tenths of a milligram—and about 0.2 gram of oil brought upon it by dropping from a rod, and *accurately* weighed. The watch-glass is now placed in an air-bath, the temperature of which remains nearly constant at 60° to 65° C. (140° to 150° F.), and heated for eight hours. It is then cooled and reweighed, the loss being figured in per cent. No oil should be passed which gives an evaporation of more than four per cent.

The following table of results upon some spindle oils shows the relation of gravity, flash point, and evaporation:

Gravity.	Flash, °F.	Evaporation.	Gravity.	Flash, °F.	Evaporation.
...	298	7.0 per cent.	.862	352	0.9 per cent.
.846	318	4.4 "	.866	366	1.7 "
...	348	2.0 "	.870	384	0.8 "
.852	348	1.0 "	.882	364	1.7 "
.856	336	1.4 "			

Notes.—The temperature employed, 65° C., is approximately that attained by a bearing (in a spinning frame) after running two hours, thus leaving the oil exposed to it for eight hours, assuming a ten-hour day.

The test is important to the insurance underwriter, because it measures the amount of inflammable material sent into the air, and hence the liability to cause or aid conflagrations; it is important to the mill-owner, as it indicates the quantity of oil left upon the bearing, hence serving its purpose.

The test is made upon other oils by heating them six hours in a shallow dish to 100°, 150°, 220°, or 300°, sometimes in a draft of air.

Cold Test.—This may be defined as the temperature at which the oil will just flow.

Manipulation.—A four-ounce vial is one-fourth filled with the oil to be examined, a short, rather heavy, thermometer inserted in it, and the whole placed in a freezing mixture. When the oil has become solid throughout, let it stand one hour; the vial is removed, the oil allowed to soften, and thoroughly stirred until it will run from one end of the bottle to the other. The reading of the thermometer is now taken by withdrawing it and wiping off the oil with waste to render the mercury visible.[1]

The *chilling point* is the temperature at which flakes or scales begin to form in the liquid, and is determined similarly, by cooling the liquid five degrees at a time.

Freezing Mixtures.—For temperatures above 35° F. use cracked ice and water; between 35° and 0° F. use two parts of ice and one part of salt; and from 0° to —30° F. use three parts of crystallized calcium chloride and two parts of fine ice or snow. A still more convenient means is by the use of solid carbonic acid dissolved in ether, giving —50° F. readily.

The preceding method is open to quite an error from the personal equation of each observer.

---

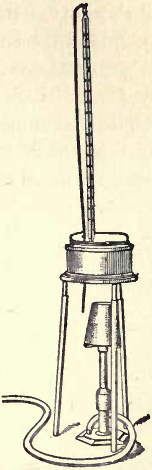
[1] Dudley and Pease, Am. Eng. and R. R. J., 69, 332 (1895).

To obviate this Martens[1] proceeds as follows:

The oil is poured into a U-tube one centimeter in diameter, sixteen centimeters high, with three centimeters between the bends, to a depth of three centimeters; it is then placed in a freezing mixture, cooled, and connected with a blast at a constant pressure of three centimeters. The temperature at which the oil begins to flow under these conditions is considered as the cold test.

Flash Point.—Several forms of apparatus for testing the flash point of lubricating oils have been devised: Pensky-Martens's closed tester employing a stirrer is used in Germany. Martens states in a later article that stirring is unnecessary. In this country, "the Cleveland cup" is extensively used. This consists (Fig. 7) of an open spun brass cup, 1⅜ inches high by 2½ inches in diameter, heated by a Tirrell burner in an air bath. The thermometer is suspended from the wire support directly over the center of the cup so that its bulb is entirely covered with oil, but does not touch the bottom of the cup.

Fig. 7.



The Cleveland Cup.

---

[1] Mitt. kgl. tech. Versuchstation; abstr. J. Soc. Chem. Ind., 9, 772 (1890).

The testing flame is a gas jet about 5 mm. in length.

The oil cup is filled with the oil to be tested to within 5 mm. of the top: the burner is adjusted to raise the temperature of the oil 5° per minute. Every thirty seconds, the testing flame is brought almost in contact with the surface of the oil. A distinct blue flame or "flash" over the entire surface of the oil shows that the flash point has been reached and the reading of the thermometer is noted. The flash point determined by "the open cup" is higher sometimes by 5°–10° than that obtained by "the closed cup."

The thermometers used should either be graduated by the maker to correct for the stem exposure with half-inch immersion in the bath or be corrected for stem-exposure. This is found by the formula,

$$\text{exposure} = d \times 0.00016\ (t - t^1);$$

d = length of exposed thread in degrees°, t, the temperature observed and t^1, the temperature of the glass of the thermometer itself as shown by a separate thermometer. This correction is additive, and if 200° were out of the bath and $t - t^1$ equal to 120°, would amount to 3.7°.

The thermometers should be frequently compared with a standard.

Fire Test.—The heating and application of the testing flame are continued as in making the flash test. The temperature is noted at which the oil ignites and burns. The flame is put out by the extinguisher supplied with the apparatus.

The method of recording is the same as in the case of the illuminating oils, one column for times and another for temperatures; the Student is recommended to read again pages 11–17. Holde[1] finds that with oils flashing between 172° C. and 241° C. the exact quantity of oil used is of little importance. In these particular cases a difference of filling of thirteen cubic centimeters altered the flash point only 1–1.5° C. For the effect of water see p. 23.

It is worthy of notice that the free acid contained in an oil lowers its flash point apparently in proportion to the quantity present.

Detection of Soap. — To increase the viscosity of an oil,[2] resort is had to the use of "oil pulp," "oil-thickener," or "white gelatin," usually an oleate of aluminium, though other bases may be present. Its disadvantages are that it causes the oil to chill more easily and to emulsify, thus increasing the friction. Furthermore, it is precipitated by contact with water or steam, causing clogging of the machinery.

The test depends upon the fact that the metaphosphates of the earthy and alkali metals and aluminium are insoluble in absolute alcohol.[3]

The test is applied as follows: Five to ten cubic centimeters of the oil to be tested are dissolved in about five cubic centimeters of 86° gasolene or ether, and about fifteen drops of the phosphoric

---

[1] J. Soc. Chem. Ind., **16**, 322 (1897).

[2] In a case which came to the writer's notice the oil would not flow out of the Saybolt "A" apparatus at 70°, at 85° required 1167″, and at 110°, 181″.

[3] Schweitzer and Lungwitz, J. Soc. Chem. Ind., **13**, 1178 (1894).

acid solution (Appendix, Reagents) added, shaken and allowed to stand; the formation of a flocculent precipitate indicates the presence of soap. An idea of the kind of soap can be often gained by adding an alcoholic solution of $PtCl_4$. If the precipitate becomes crystalline it is a potash soap; if it dissolves, soda, lime, or magnesia; if unchanged, alumina or iron.

For the accurate determination of these compounds a known weight of the oil must be ignited, the residue determined and quantitatively examined.

Caoutchouc.—Holde[1] states that one to two per cent. of unvulcanized caoutchouc is sometimes added to oils to increase their viscosity. This may be detected by adding three parts of alcohol to four parts of the ethereal solution, whereby the rubber material is precipitated and may be dried and weighed.

Tests for Antifluorescents.[2,3]—It is often desired to remove the fluorescence or "bloom" from petroleum oils. This may be effected by refining with chromic acid, or more easily by the addition of a small quantity of nitro-naphthalene or nitro-benzene. The latter may often be detected by the odor.

The test is made by boiling about one cubic centimeter of the oil with three cubic centimeters of ten per cent. alcoholic potash for one to two minutes. If either of the nitro compounds be present, a blood or violet-red coloration is produced: a

---

[1] Holde-Mueller, "Examination of Hydrocarbon Oils" (1915), 166.
[2] Holde, J. Soc. Chem. Ind., **13**, 906 (1893). [3] Brooks & Bacon J. I. & E. C. **6**, 623 (1914).

pure mineral oil is changed only to yellow or brownish-yellow by this treatment. In case the characteristic color does not appear the following test may be applied.[1] It depends upon the reduction of the nitro bodies to their amines.

A few cubic centimeters of the oil are heated with feathered tin and hydrochloric acid in an Erlenmeyer flask for ten minutes: this can be aided by the introduction of a piece of platinum wire. The oil is separated by a separatory funnel and filtration through a wet filter, the filtrate treated in another separatory with sodium hydrate until the tin hydrate redissolves and shaken out with 10–20 cc. of ether. The amines go into solution in the ether, giving to it a violet color and fluorescence in the case of α-napthylamine. These can be recognized by their odor, that of napthylamine being very characteristic. The latter may be recognized by dissolving in hydrochloric acid, evaporating the latter, and upon treatment with ferric chloride obtaining an azure-blue precipitate. This changes when filtered off to purple-red and the filtrate to violet.

Aniline can be recognized by solution in concentrated sulphuric acid and the red and then blue color which appears on the addition of a small crystal of potassium bichromate. Free aniline is also temporarily colored violet by a solution of bleaching powder.

---

[1] Holde-Mueller, op. cit., 168.

To ascertain if an oil be fluorescent, place a few drops upon a piece of hard rubber or other black surface and observe if any trace of blue color be perceptible.

Test for Fatty Oils.—To detect small quantities of fatty oil (one-quarter to two per cent.) Lux[1] recommends heating a few cubic centimeters of the oil for fifteen minutes with some bits of sodium in a test-tube in an oil-bath; a similar test is made with sodium hydrate. The temperature employed should be for light oils about 230°, for dark oils 250°.[2] In case fatty oil be present, the contents of one or both of the tubes solidify to a jelly of greater or less consistence according to the amount of fatty oil present.

The quantitative determination of these oils, as for example in cylinder oils, is effected after the manner of determining the saponification value (p. 65) or the detection of unsaponifiable oils in fatty oils (p. 68).

Schreiber[3] adopts a similar method to Sweetham and Henriques, in that he dissolves 5 grams of the oil in 25 cc. of benzole, adds 25–50 cc. $\frac{N}{2}$ alcoholic potash, and boils for half an hour on the water-bath, using a three-foot glass tube as a condenser.

Gumming Test.[4]—This is designed to give an idea of the amount of change that may be expected

---

[1] Z. anal. Chem., 24, 357 (1885).
[2] Holde-Mueller, op. cit., 160.
[3] J. Am. Chem. Soc., 29, 74 (1907).
[4] Gill, J. Am. Chem. Soc., 24, 467 (1902).
Chiefly applicable to Paraffine base oils.

in a mineral oil when in use. The resinified products formed, increase the friction of the revolving or rubbing surfaces.[1] It is also a measure of the amount that an oil will "carbonize" in a gas or gasolene engine cylinder. It is applied after the manner of the Elaidin Test, by thoroughly mixing together five grams of the oil in a cordial glass with eleven grams of nitrosulphuric acid and cooling by immersion in a pan of water at 10°–15°. Brownish spots or, in case of a bad oil, masses, form around the edges and become red in the course of two hours. The cordial glass is filled successively three times with 70°–86° naphtha and the oil dissolved off the surface of the acid, the gasolene solution being sucked off into a bottle with an air-pump. Care is taken not to suck off any of the tarry matter formed. The acid can be neutralized with ammonia and the tar can be collected on a tared filter, washed with gasolene that leaves no residue on evaporation, dried at a low temperature, and weighed as gummy matter. As shown by long practical experience, the oil showing the least tar or gum is the best oil; it also absorbs the least oxygen.

Carbon Residue Test.[2]—The apparatus used in this test is a glass retort of approximately 100 cc. capacity, with a plain glass tubulature for a cork stopper. A ground-glass tubulature will not do, because heat will break it. These retorts are fur-

---

[1] Aisinman, J. Soc. Chem. Ind., 14, 282 (1895).

[2] Souther, Proc. Am. Soc. Testing Materials, 8, 593 (1908). The results of this test are comparative only when it is made by the same operator.

nished by the Bausch and Lomb Optical Co., and known as No. 16,384 Special.

The method of operation is as follows: Clean the retort carefully, and heat it over a Bunsen burner to remove moisture. When cool, suspend it from a balance by a light wire and weigh into it about 40 grams of oil. Distil over a Bunsen burner, with a cork stopper loosely fitted in tubulature. Commence distillation with the flame high enough to distil the 40 grams in about 30 minutes or at the rate of from 40 to 50 drops per minute. The rapidity of distillation can be determined from the rate of dropping of the oil.

A slight smoky vapor will accompany the distillate at the rate above mentioned. Toward the finish, during the removing of the last trace of liquid oil, the rapidity of dropping will diminish to a very few drops per minute.

Continue distillation until the residue in the bottom of the retort is nearly dry. Increase the Bunsen flame to its full extent and apply it all around the sides and neck of the retort until the oil condensed on the sides is also driven over. To accomplish this it will be necessary to blow the vapor out of the retort several times by removing the cork and blowing through the tubulature.

Then hold the retort over a blast lamp with a flame hot enough to wrinkle the glass but slightly. Continue this heating until all traces of oil are burned off, leaving only the carbon residue in the bottom of the retort.

The end-point of the determination is clear. All except the desired carbon residue will disappear very rapidly under this treatment. The carbon residue itself will begin to curl up if heated too strongly. The heating must be continued only long enough to dry the carbon residue proper. This is very easy if the amount of residue is small, and requires strong heating. Heating must be stopped before the carbon begins to burn even on the edges.

When the retort is cool, weigh it again and determine the percentage of residue, as compared with the original weight of the oil.

Oils showing more than 0.50 per cent. of coke-like residue are not suitable for automobile engine work. The best of them contain 0.06 to 0.08 per cent.; a large number contain 0.20 to 0.40 per cent. and are entirely satisfactory. Steam engine cylinder oils contain in the neighborhood of 4.00 per cent. and cannot be used.[1]

Gasolene Test.—This shows the presence of tar (still bottoms) or asphaltic matters.

Mix 10 cc. of the oil with 90 cc. 86°–88° gasolene (from Pennsylvania crude) Bpt 30°–50° C., allow to stand one hour at 70° to 80° F.: not more than ten per cent. of flocculent or tarry matter should have settled out. If the test be applied to the oil before making the flash test and then again after this test it shows the extent to which the oil is changed upon heating. Other things being equal the oil which is changed the least is the best oil.[2]

Microscopical Test.—Put a few drops of the well

---

[1] Gray uses a 30 cc. quartz boiling flask for this determination, Proc. A.S.T.M., 1914, 364.

[2] Conradson, J. Ind. and Eng. Ch., **2**, 171 (1910).

mixed oil on a slide and note the nature of the suspended matter—whether carbonaceous specks, flakes of paraffine, which disappear on warming, or foreign matter. A good oil should be practically free from all these bodies.

Heat Test.—Heat 20–25 cc. of the oil in an Erlenmeyer flask or beaker nearly to the flashing point and keep it at this temperature for fifteen minutes; a satisfactory oil will darken, but remain clear even after standing a day. A poorly refined oil changes to jet black, and forms a carbon-like precipitate. This is usually indicative of an oil that has been refined by acid treatment.

Herschel's Demulsibility Test.[1]—The test is applicable to non-emulsifying oils, such as are used with high speed engines and turbines, and in its present form does not apply to steam cylinder or other compounded oils. It is made as follows:

Twenty cc. of oil and 40 cc. of distilled water are placed in a 100 cc. cylinder having an inside diameter of 2.6 cm. and heated to 55°. The oil and water are then mixed or emulsified by stirring with a paddle for five minutes at a speed of 1500 R. P. M. The paddle is simply a metal plate 89 by 20 by 1.5 mm. thick, conveniently driven by an electric motor.

The rate at which the oil settles out from the emulsion, when it is allowed to stand at a temperature of 55° is a measure of the emulsibility of the oil. There is a tendency for the rate of settling out of the oil to increase up to a maximum and then

---

[1] U. S. Bureau Standards Bulletin 86 (1917).

decrease, and we may take readings every five minutes (or every minute if the oil separates out rapidly) and note the maximum rate. For example, the following readings were obtained for a certain oil:

Time	Time Since Stopping Paddle	Reading of Cylinder at Top of Emulsion	Cc. of Oil Settled Out	Rate of Settling, Cc. per hr.
9.50	0	60	0	0
9.55	5	57	3	36
10.02	12	47	13	65
10.05	15	43	19	68
10.10	20	41	17	57

The maximum rate is here 68 cc. per hour, and this is called the "demulsibility." The best transformer, motor, and turbine oils settle out in one minute or less, so that if we take readings to even minutes and even cc., the rate would be 1200. Oils are found with rates all the way down from this maximum rate to zero.

It has been found necessary to shake the container holding the sample of oil if it has been allowed to stand for some time, or otherwise the oil poured off from the top may show a different rate of settling from the oil at the bottom. It is also necessary to protect the oil from sunlight which has the effect of decreasing the rate of settling.

With some oils, under certain conditions, part of the water does not enter into the emulsion and drops of oil adhere to the sides of the cylinder. When this phenomenon occurs, the rate of settling, indicated by the test, is apt to be incorrectly high. The adhering drops may be avoided by using a lower speed or less water, the total quantity of oil and water being kept equal to 60 cc. If part of the water does not enter into the emulsion, but we do not have the above described phenomenon, complete emulsification may sometimes be obtained by prolonging the stirring beyond five minutes, or by increasing the speed.

Friction Tests.—The writer is inclined to doubt if friction tests are worth the outlay for a machine and the time expended in their execution. Without question they do determine the relative efficiency as regards lubricating power of different oils, but the conditions under which the test is made seldom occur in practice; the bearings upon which the oil is tested are as nearly perfect as can be made, and the feed and load are as regular as is possible; in other words, the conditions are ideal.

The lubricating power of an oil is so closely related to its viscosity[1] that the author believes that results of more practical value can be obtained by the determination of the viscosity of the oils, and subsequent observation of their behavior in actual use, than by the longer and more troublesome friction test. Recent experiments,[2] however, have shown that of two oils of the same viscosity and other constants, the coefficient of friction of one was 14 per cent. less than the other.

In case, however, it be desired to make the

---

[1] Brannt, "Petroleum and its Products," p. 510; Woodbury, *vide infra.*

[2] Jour. Am. Soc. Mech. Eng., 32, 834 (1910).

friction test, the following machines, it is believed, will be found to be most satisfactory for the purpose:

For spindle oils and light lubricating oils, the machine[1] of the Thurston type which can be run at the highest speed and lowest pressure.

For heavy oils and railroad work, the large machine of the Thurston[2] type, described in his "Friction and Lost Work in Machinery and Millwork," p. 254; also in Brannt, p. 486; also in Archbutt and Deeley.[2]

---

[1] Made by Olsen or Riehlé Bros., Philadelphia, Pa.

[2] "Lubrication and Lubricants," 1912, pp. 370–416, Chapter IX.

CHAPTER III.

ANIMAL AND VEGETABLE OILS.

THE tests most commonly employed for the identification of these oils are as follows: specific gravity, refractive index, Valenta test, elaidin test, Maumené test, heat of bromination test, iodine number, and saponification value.

These last two "numbers" have been refined[1] so that a single drop 0.03 gram suffices for their execution.

In addition certain special and commercial tests are applied, as Bechi test, Baudouin test, free acid, spontaneous combustion and drying test.

Specific Gravity.—This is usually determined either by the Westphal balance (p. 34) or by the *picnometer*.

A two-necked flask of fifty cubic centimeters' capacity, having a thermometer carefully ground into one neck, the second one being a narrow tube bearing the mark is most suitable. This is filled with the oil to be examined, cooled to 15.5° C.,[2] the excess of oil removed and weighed. If the weighings be made to 0.5 milligram and corrections applied, the determination is accurate to 0.00002.[3]

For the determination of the specific gravity of small quantities of oil, the aræopicnometer of Eichhorn[4] may be used. Still more satisfactory results can

---

[1] Gill and Simms J. I. & Eng. Chem. 13, 547 (1921).

[2] Allen (Organic Analysis, 33) states that a correction of 0.00069 can be made for each variation of 1° C.

[3] Wright, J. Soc. Chem. Ind., 11, 300 (1892).

[4] Fres. Zeit. 30, 216 (1891).

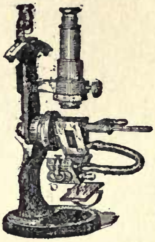
be obtained by weighing one or five cubic centimeters of the oil carefully measured from an accurately calibrated pipette. Or a mixture of alcohol and water can be made until a drop of oil will stay in any position in it, and its specific gravity determined.

Refractive Index.—This is of the same value as the determination of specific gravity; it has, however, the advantage that it is more rapid and uses only one or two drops of the oil.

The Abbè refractometer, Fig. 8, the prisms of which are kept at constant temperature, usually 25° C., by circulating water is best adapted.

The illuminating mirror should light the cross hairs and the telescope should be sharply focused on them.

FIG. 8.



Refractometer.

The double prism is opened by means of the screw heads, and after carefully cleansing the prisms with cotton and ether, a drop or two of the oil placed on the horizontal surface of the fixed prism. The prisms are then tightly closed. The telescope is brought into the position shown and the sector is firmly held and the alidade (the moving part) moved forward until the field of vision shows the boundary between light and shade just intersecting the cross hairs.

By means of the screw on the right of the instrument, this boundary line should be made as sharp as possible. The index of refraction is read off directly from the sector, using a lens if necessary; the reading is accurate to .0002.

After using, the prisms are again carefully cleansed and a piece of filter paper placed between them to prevent them from being scratched. The instrument is in correct adjustment when water at 18° gives a mean reading of 1.333. The temperature correction for oils and fats is 0.0004 for every degree rise.

Valenta Test.[2]—Although considered by some to be unreliable, yet as the indication given by this test may be of value, it is barely worth the trouble of execution. It depends upon the solubility of the oil in glacial acetic acid.

Enough oil is poured into a test-tube to fill it to the depth of about one inch, the exact height being marked by the thumb; an equal quantity of glacial acetic acid is poured in, that is, until the acid reaches the point indicated by the thumb. A light thermometer is placed in the tube, and it is heated until the oil dissolves,—shown by the liquid becoming homogeneous. The tube is now allowed to cool, and the point noted at which it begins to become thoroughly turbid.

Castor oil is soluble at ordinary temperatures, while rape-seed[3] and other cruciferous oils are usually insoluble even at the boiling point of the acid. The temperatures at which other oils become turbid are given in Table X.

---

[1] Z. anal. Chem., 30, 216 (1891).

[2] Valenta, Dingler polyt. J., 253, 418; also J. Soc. Chem. Ind., 3, 643 (1884).

[3] American rape oils behave differently from European, in being more soluble.

Elaidin Test.—Although this is not a quantitative test, yet its ease of application and the conclusions which may be drawn from it render it valuable. It depends upon the change of the liquid olein into its solid isomer elaidin, and is especially applicable to olive and lard oils.

Manipulation.—Five grams of the oil are weighed[1] —within two drops—into a cordial glass, 7 grams of nitric acid, sp. gr. 1.34, are then weighed into it,[1] and two pieces of wet copper wire, freshly cleansed with dilute nitric acid and (0.6 to 1.0 gr.) added. Place the glass in a pan of cold water at about 12° C., and stir with a short glass rod about twenty to thirty turns, not only with a rotary movement but also with an up-and-down motion, so as to mix the oil and the evolved gas thoroughly. When the wire has dissolved, add a third piece and stir as before. This third addition should furnish gas enough if the liquid has been kept cool and the stirring has been thorough.

At the end of the first hour pure lard oil will usually show flakes of a wax-like appearance, and upon standing without disturbance and at the same temperature for another hour, the oil will have changed to a solid white cake hard enough to bear several ounces' weight or admit of lifting the glass and contents by the glass rod.

Most of the fish and seed oils yield a pasty or buttery mass separating from a fluid portion,

---

[1] Not on the analytical balance.

whereas olive, almond, peanut, lard, sperm, and sometimes neat's-foot oil, yield a solid cake.

Instead of using nitric acid and copper, sulphuric acid of 46° Baumé, containing a little nitric acid and saturated at 0° C. with nitric oxide, may be employed.

A test should always be made at the same time with an oil of undoubted purity.

Notes.—If the oil be stirred too much or too frequently, or is too warm, it has no opportunity to form a hard cake.

Hübl states that all attempts to make the test a quantitative one have resulted in failure.

Mercury can be used instead of copper.

Cailletet's method,[1] in which a smaller quantity of oil is used and sulphuric and nitric acids allowed to act upon it in a boiling water-bath, cannot, in the experience of the writer, be depended upon to give reliable results.

Maumené Test.[2]—While this, like the preceding, is not a quantitative test, yet the indications afforded by it are of more value in many cases than those obtained by quantitative methods, as, for example, the saponification value. It depends upon the heat developed by the mixing of the oil with strong sulphuric acid. This takes place in a small beaker seven and one half to nine centimeters deep and of one hundred and fifty cubic centimeters' capacity, packed in an agate-ware cup with dry felt or cotton waste packing.

---

[1] Milliau, J. Am. Chem. Soc., **15**, 156 (1893).

[2] SO_2Cl gives similar results.

Manipulation.—Fifty grams of the oil are weighed[1] into the beaker to within two drops, and its temperature noted by a thermometer. Ten cubic centimeters of sulphuric acid are now run gradually into the oil,—allowing the graduate to drain five seconds,—the mixture being stirred at the same time, and the stirring continued until no further increase in temperature is noted. The highest point at which the thermometer remains constant for any appreciable time is observed, and the difference between this and the initial temperature is the "rise of temperature." This varies with the strength of the acid employed, and to secure uniformity[2] the results should be expressed by dividing the rise of temperature with the oil by the rise of temperature with water, and multiplying by one hundred. This is called the "specific temperature reaction." The rise of temperature with water is determined in the same manner as with oil, using the same vessel.

Notes.—In performing this test it is important that the oil and acid be of the same temperature, attained by keeping them beside each other.

The strength of acid should be as far as possible the same; it should be determined not by specific gravity, but by titration, as one hundred per cent. and ninety-four and three-tenths per cent. acid have the same specific gravity.

---

[1] Not on the analytical balance.

[2] Tortelli, J. Soc. Chem. Ind., **23**, 668 (1904), is unable to secure uniformity in this way.

For concordant results the conditions should be the same, and the same apparatus should be used. In case the test is to be applied to a drying oil, it should be diluted one-half with a mineral oil, 25° paraffine, for example, thoroughly mixing them. The "rise of temperature" is then, the rise of temperature of mixture minus half the rise of temperature of fifty grams of mineral oil, multiplied by two.

It is advisable to make a test at the same time with an oil of known purity. Results should agree within two per cent. By the use of the Hübl formula, p. 66, substituting thermal values, results comparable with those obtained with the iodine value can be obtained.

Sherman, Danziger, and Kohnstamm[1] have studied this method with the idea of eliminating the errors. Rather than dilute the oil with a mineral oil they dilute the acid, using one of eighty-nine per cent. The results obtained are a little lower for vegetable oils and a little higher for animal oils than those usually found with the strong acid as employed by Thomson and Ballantyne. Mitchell[2] uses an inert diluent—carbon tetrachloride—in a vacuum-jacketed tube and one-fifth the quantities; all oils are diluted. He finds that the results obtained are in close agreement with the bromine thermal values; further, that the test may be of use in determining the degree of oxidation of fats and oils, the figures becoming greater with the age of the oil.

---

[1] J. Am. Chem. Soc., **24**, 266 (1902).

[2] Analyst, **26**, 169 (1901).

Data upon various oils will be found in Table X.

REFERENCES.

MAUMENÉ, Compt.-Rend., **35**, 572 (1852).
ELLIS, J. Soc. Chem. Ind., **5**, 361 (1886).
THOMSON and BALLANTYNE, J. Soc. Chem. Ind., **10**, 234 (1891).
RICHMOND, Analyst, **20**, 58 (1895).
MUNROE, Am. Pub. Health Ass'n, **10**, 236 (1884).

Heat of Bromination Test. — This test, which was proposed by Hehner and Mitchell,[1] consists in observing the rise of temperature when bromine is added to a solution of the oil in chloroform. It occupies a middle position between the Maumené, being more accurate than it, and the Hübl, than which it is less delicate; by multiplying by a factor, different for each instrument, the results obtained can be expressed in figures, which are a close approximation to those obtained by the Hübl method.

The process has not found extensive application, and for a description of the method of execution reference may be had to articles by Wiley, J. Am. Chem. Soc., **18**, 378 (1896), and Gill and Hatch, id., **21**, 27 (1899).

Iodine Number or Value. — This is the percentage of iodine absorbed by an oil; the method depends upon the fact that different oils absorb different amounts of the halogens; the process is mainly one of addition, although small quantities of substitution products are formed. For example, the unsaturated body olein, $(C_{17}H_{33}COO)_3C_3H_5$,

---

[1] Analyst, **20**, 146 (1895).

when brought in contact with iodine takes up six atoms and forms the *addition product*, di-iodo stearin, $(C_{17}H_{33}I_2COO)_3C_3H_5$. Palmitin, $(C_{15}H_{31}COO)_3C_3H_5$, when similarly treated, forms no addition product, but a small quantity of the *substitution product*, iodo-palmitin, $(C_{15}H_{30}ICOO)_3C_3H_5$, and the hydrogen displaced unites with the iodine to form hydriodic acid. The quantity of hydriodic acid thus formed is a measure of the amount of substitution.[1]

1. Hanus's Method.—*Manipulation.*—From 0.12 to 0.15 gram of a drying oil, 0.2 to 0.3 gram of a non-drying oil, or 0.6 to 0.7 gram of a solid fat, is accurately weighed into a *dry* two hundred cubic centimeter bottle. This should be of colorless glass and be provided with a well-ground stopper. This is best effected by pouring out about five grams of the oil into a No. 1 beaker containing a short stirring rod, and setting it into a watch-glass upon the pan of the analytical balance. The whole system is weighed, the beaker removed, and several drops of oil transferred to the bottle by dropping down the rod, being careful that no oil touches the neck. Eight drops are approximately 0.2 gram. The beaker is replaced in the watch-glass and the system again weighed, the difference in weight being the amount of oil in the bottle.

The oil is dissolved in 10 cc. of chloroform, 30 cc. of the iodine solution (Appendix, "Reagents") added,—best from a burette,—and allowed to

---

[1] McIlhiney, J. Am. Chem Soc., **16**, 275 (1894).

stand with occasional shaking for exactly fifteen minutes; with oils of an iodine number of less than 100, ten minutes suffices; 15 cc. of potassium iodide solution[1] are added and the solution titrated, with or without the addition of starch, with sodium thiosulphate until the halogen disappears.

At the same time at which the oil was prepared two "blanks" should be prepared similarly in every way to the actual tests, except in the addition of the oil, and treated in every respect like them; the strength of the thiosulphate solution should also be determined the same day on which this test is carried out.

Standardization of the Thiosulphate Solution.—Ten cubic centimeters of potassium iodide and one hundred cubic centimeters of water are poured into the Erlenmeyer flask; twenty cubic centimeters of the bichromate solution, equivalent to 0.2 gram of iodine, are now measured in with a pipette, and to this five cubic centimeters of strong hydrochloric acid added and the mixture shaken for three minutes. It is now titrated with the thiosulphate solution until the yellow color of the iodine has almost disappeared; starch paste is now added, and the titration continued until the deep-blue color of the solution changes to a sea-green,—due to $CrCl_3$,—which is usually brought about by the addition of a single drop.

The reactions involved are:

---

[1] This is the original method. Tolman adds here 100 cc. water as in the Hübl method.

$$K_2Cr_2O_7 + 14HCl = 2CrCl_3 + 2KCl + 7H_2O + 3Cl_2;$$
$$3Cl_2 + 6KI = 6KCl + 3I_2;$$
$$6Na_2S_2O_3 + 3I_2 = 3Na_2S_4O_6 + 6NaI.$$

Notes.—Wijs[1] uses iodine chloride instead of bromide; it is more troublesome to prepare and gives results about 1.2 points higher.[2] Either of these methods has the advantage over Hübl's,—first, that the solutions keep better, remaining practically unchanged for several months; secondly, that the action is about sixteen times as rapid, it being completed in fifteen minutes; thirdly, that the solutions are cheaper.

Acetic acid cannot be displaced by carbon tetrachloride as a solvent, as the last traces of iodine are difficult to remove from it. The acetic acid used should be at least 99.5 per cent. and show no reduction with potassium bichromate and sulphuric acid.

2. HÜBL'S METHOD.—*Manipulation.*—The oil is weighed out as in 1, into three hundred cubic centimeter bottles, except that about twenty-five per cent. more may be used.

The oil is now dissolved in ten cubic centimeters of chloroform, thirty cubic centimeters of iodine[3] and mercuric chloride solution[3] added, the bottle placed in a dark closet, and allowed to stand, with occasional gentle shaking, for four hours. If the solution becomes nearly decolorized after two hours, an additional quantity should be added.

---

[1] Berichte, 31, 752 (1898).

[3] See Appendix Reagents.

[2] Tolman and Munson, J. Am. Chem. Soc., 25, 244 (1903). See Appendix, Table XIII.

One hundred cubic centimeters of distilled water and twenty cubic centimeters of potassium iodide are added to the contents, and the excess of iodine titrated with sodium thiosulphate. If at this point a red precipitate (HgI_2) is formed, more potassium iodide should be added. As the chloroform dissolves some of the iodine, the titration can proceed until the chloroform layer is nearly colorless, then the starch solution is added, and the operation continued to the disappearance of the blue color.

"Blanks" should be titrated as with the foregoing process, page 61.

Notes.—The method was proposed by Cailletet in 1857, made use of by Mills and Snodgrass[1] in 1883, using, however, bromine and carbon bisulphide, and described in almost its present form by Hübl.[2] The chief factors in its execution are (1) strength of the iodine solution; (2) the quantity used; and (3) the length of its time of action.

1. *The Strength of Iodine Solution.*—According to Hübl's original memoir, the solutions can be kept indefinitely when mixed.

Fahrion[3] states that the solution deteriorated as much as from seventeen to twenty-three per cent. in eight days. Ballantyne[4] confirms the deterioration, but finds it much less, five to eight per cent.

---

[1] J. Soc. Chem. Ind., **2**, 435 (1883).

[2] Dingler polyt. J., **253**, 281; also J. Soc. Chem. Ind., **3**, 641 (1884).

[3] J. Soc. Chem. Ind., **11**, 183, abstr. (1892).

[4] Id., **13**, 1100, abstr. (1894).

in thirty-eight days. This weakening of the solution is probably due to the hydriodic acid formed by the action of the iodine upon the alcohol.[1]

The mercuric chloride acts apparently as a carrier of iodine, as the reaction takes place very slowly without it. (Gantter.)[2] Waller[3] finds that the addition of fifty cubic centimeters HCl, specific gravity 1.19, to the mixed iodine solution preserves it for months. Of the other metallic chlorides, $CoCl_2$ gives the highest true iodine value, $MnCl_2$, $MnBr_2$, and $NiCl_2$ cause practically no addition. (Schweitzer and Lungwitz.)[4]

2. *The Quantity of Iodine Solution used.* — The mixed iodine solution as made up should require about fifty-three cubic centimeters of the thiosulphate. Before using, a rough titration should be made, and if it be much weaker than this, a proportionately larger amount added. The action of a large excess of iodine is to increase the substitution rather than addition; increase in temperature or in time produces the same effect.[5]

The excess of iodine recommended is from one hundred and fifty to two hundred and fifty per cent.; some observers recommend from four hundred[6] to six hundred per cent.[7]

---

[1] J. Soc. Chem. Ind., **14**, 130 (1895).
[2] Id., **12**, 717, abstr. (1893).
[3] Chem. Ztg., **19**, 1786, 1831 (1895).
[4] J. Soc. Chem. Ind., **14**, 1031 (1895).
[5] J. Soc. Chem. Ind., **12**, 717, abstr. (1893).
[6] Id., **14**, 1031 (1895).
[7] Holde, Mitt. kgl. Techn. Versuchs., **9**, 81 (1891).

3. *Length of Time.*—Two hours is sufficient for olive oil, tallow, and lard, while for linseed oil, balsams, and resins twenty-four hours should be allowed.[1]

Waller[2] thinks that the "iodine number" is really the sum of changes in the fat due to absorption of iodine, oxygen, and chlorine.

The two latter come from the interaction of the iodine, and mercuric chloride setting free chlorine, which sets free some oxygen from the water.

Schweitzer and Lungwitz[3] obtain what they term "the true iodine value" by acting upon the oils for twenty-five minutes at 45° C. with iodine dissolved in carbon bisulphide and in the presence of a considerable quantity of mercuric chloride. Practically no hydriodic acid is formed under these conditions, and yet in the case of oleic acid it absorbs more than the theory requires.

They have studied further the effect of various solvents for iodine instead of ethyl alcohol, as methyl alcohol, ether, carbon tetrachloride and bisulphide.

Ingle[4] has shown that the free acid formed during the process is due to the action of water upon the iodochlorides. Some of these are reduced by potassium iodide with liberation of iodine and consequent reduction in the iodine absorption. Iodine chloride is the active agent, and not hypoiodous acid.

---

[1] Dieterich, J. Soc. Chem. Ind., **12**, 381 (1893).
[2] Analyst, **20**, 280, (1895).
[3] J. Soc. Chem. Ind., **14**, 1031 (1895).
[4] J. Soc. Chem. Ind., **21**, 587 (1902).

Gill and Adams,[1] using a solution of iodine and mercuric iodide in absolute methyl alcohol, have diminished the amount of substitution that takes place. Oleic acid added the theoretical amount of iodine, and even stearic acid about seven per cent.

For the calculation of the percentage of adulteration of one oil by another, Hübl gives the following formula:[2]

"Let x=percentage of one oil and y=percentage of the other oil, further, m=iodine value of pure oil x, n of pure oil y, and I of the sample under examination, then

$$x=\frac{100\ (I-n)}{m-n}."$$

He further states that the age of the oil, provided it be not rancid or thickened, is without influence on the iodine value. Ballantyne[3] finds that light and air diminish the iodine number.

As might be expected, the iodine value is inversely proportional to the cold test.

The method, as will be seen, is a conventional one, and the best results will be obtained by using measured quantities of reagents and carrying through the process in the same manner every time.[4]

The calculation is perhaps most easily made as follows: Subtract the number of cubic centimeters

---

[1] J. Am. Chem. Soc., **22**, 13 (1900).

[2] Dingler polyt. J., **253**, 281 (1884).

[3] J. Soc. Chem. Ind., **10**, 31 (1891).

[4] If, for example, the water be added before the iodide solution, the iodine number is changed by 0.3 per cent.

of thiosulphate used for the titration of the oil from that obtained by titrating the blank,—this gives the thiosulphate equivalent to the iodine absorbed by the oil. Multiply this number (of cubic centimeters) by the value of the thiosulphate in terms of iodine, and the result is the number of grams of iodine absorbed by the oil; this divided by the weight of oil used and multiplied by one hundred gives the iodine number.

In case it be desired to recover the iodine used, reference may be had to an article by Dieterich, abstracted in the Jour. Soc. Chem. Ind., **15**, 680 (1896).

Oxidized Oils—Iodine Number of.—To find the original iodine number of a semi-drying or non-drying oil which has been altered by atmospheric oxidation, add 0.8 to the iodine number found on the altered sample for each increase of 0.001 in the specific gravity $\left(\text{taken at } \frac{15.5° \text{ C.}}{15.5° \text{ C.}}\right)$[1].

Bromine Number or Value.—The iodine method just described has, among others, the disadvantage that it fails to distinguish between addition and substitution; this is sometimes of importance, and to accomplish it McIlhiney[2] makes use of the bromine absorption.

Manipulation.—From 0.2 to 0.3 gram of a drying oil, 0.4 to 0.5 of a non-drying oil, or 1.0 to 1.2 grams of a solid fat, are accurately weighed into the

---

[1] Sherman and Falk., J. Am. Chem. Soc., **27**, 608 (1895).

[2] J. Am. Chem. Soc., **21**, 1084 (1899).

three hundred cubic centimeter bottle, as in the iodine number (page 62).

The oil is dissolved in ten cubic centimeters of carbon tetrachloride, and twenty cubic centimeters of bromine solution (Appendix, Reagents) added, best from a burette. After allowing it to stand two minutes by the watch, twenty or thirty cubic centimeters of potassium iodide are added, in the manner described below, the amount depending upon the excess of bromine. To prevent loss of bromine and hydrobromic acid, a short piece of thin and wide rubber tubing—"bill tie tubing"—is slipped over the lip of the bottle, thus forming a well around the stopper; some of the iodide solution is poured into this and the bottle cooled in cracked ice. Upon removing the stopper the solution is sucked into the bottle, it is shaken to insure the solution of the vapors, and the remainder of the reagent added. The iodine liberated is titrated by sodium thiosulphate in the usual way.

When this titration is finished, five cubic centimeters of the potassium iodate solution are added and the titration repeated. The iodine liberated in this reaction is equivalent to the hydrobromic acid present. Blank determinations should be made with the reagents used, as with the iodine number.

Notes. — Oftentimes, particularly with resins, emulsification of the solution takes place, masking the end point. This can be prevented by the addition of fifty or a hundred cubic centimeters of a ten per cent. solution of salt.

In case ice be not at hand, the vapors will probably be completely absorbed by passing through the iodine solution in the rubber well.

The reactions involved, in addition to those on pages 60 and 62, are:

Palmitin.

$$(C_{15}H_{31}COO)_3C_3H_5 + 3Br_2 = (C_{15}H_{30}BrCOO)_3C_3H_5 + 3HBr.$$

$$3HBr + 3KI = 3KBr + 3HI.$$

$$6HI + KIO_3 = 3I_2 + 3H_2O + KI.$$

The calculation is similar to that followed in the iodine number (page 66).

The percentage of bromine found as hydrobromic acid is called the bromine substitution figure, and the total percentage absorbed, less twice the bromine substitution figure, gives the bromine addition figure.

The method has the further advantages that it is rapid, the bromine solution is permanent and inexpensive. For data upon various oils, see Table XIV.

Saponification Value.—This is expressed by the number of milligrams of potassium hydrate necessary to saponify one gram of the oil. It is called from the originator "Koettstorfer[1] number or value," also "Saponification number," and must not be confounded with "Saponification *equivalent*" as proposed by Allen,[2] which is the number of grams of oil saponified by 56.1 grams of potassium hydrate.

Manipulation.—One to two grams of the oil are weighed out into a two hundred cubic centimeter

---

[1] Z. anal. Chem., **18**, 199 (1879).

[2] Commercial Organic Analysis, **2**, 40.

Erlenmeyer flask (as in the iodine value, *q. v.*, page 60) and saponified by twenty-five cubic centimeters $\frac{N}{2}$ alcoholic potash accurately measured from a burette, by heating upon a water-bath, a one-inch funnel being inserted in the flask.

When the saponification is complete, shown by the homogeneity of the solution, a few drops of phenolphthalein are added and the excess of alkali titrated with $\frac{N}{2}$ hydrochloric acid. Two blank determinations of the strength of the $\frac{N}{2}$ potassium hydrate must be made simultaneously, by heating 25 c.c. under the same conditions as when mixed with the oil and for the same length of time.

Notes.—Many prefer to cork the flasks tightly and tie down the stoppers, thus saponifying under pressure; others make use of a return flow condenser, oftentimes merely a long glass tube.

Smetham[1] adds twenty cubic centimeters of ether and finds that it aids saponification. Henriques[2] uses three to four grams of oil, twenty-five cubic centimeters of petroleum ether, and twenty-five cubic centimeters of *normal* alcoholic potash, saponifying in the cold by allowing to stand over night; the advantage consists in preventing the change in the solution by boiling.

McIlhiney[3] has applied the process to dark-colored substances by making use of the principle

---

[1] Analyst, **18**, 193 (1893).

[2] Z. angew. Chemie, 721 (1895).

[3] J. Am. Chem. Soc., **16**, 409 (1894). For a discussion of the theory of the process, see Lewkowitsch, J. Soc. Chem. Ind., **17**, 1107 (1898).

that when ammonium chloride is added to a neutral soap solution, and the mixture distilled, the amount of ammonia freed is equivalent to the quantity of alkali combined with the fatty acids. As a description of the process is beyond the scope of the present volume, reference must be had to the original article.

As ordinarily prepared, the alcoholic potash solution turns rapidly reddish-brown, so that it is very difficult to note the end point. This trouble can be partially avoided by adding a drop or two of the solution to the diluted indicator contained upon a tile after the manner of the titration of iron by bichromate. As the color is probably due to the polymerization of the aldehyde formed by the oxidation of the alcohol, it is more satisfactory to use for the preparation of the potash solution an alcohol which is practically aldehyde free. This is best made, according to Dunlap,[1] as follows: one and one-half grams of silver nitrate are dissolved in 3 cc. water, added to one liter of alcohol and thoroughly shaken; three grams of potassium hydrate are dissolved in 15 cc. warm alcohol and, after cooling, added to the alcoholic silver nitrate and thoroughly shaken again, best in a tall bottle or cylinder. The silver oxide is allowed to settle, the clear liquid siphoned off and distilled. Alcoholic potash made up from this, using the so-called "potash by alcohol," will give a solution which will remain water-white for weeks.[2]

---

[1] J. Am. Chem. Soc., 28, 397 (1906).

[2] As it will if kept under an atmosphere of hydrogen.

It should be noted that glycerides of acids of low molecular weight have high saponification values; *e.g.*, acetin $C_3H_5(COOCH_3)_3$ (Molec. Wt. 218) has S. V. 772.

Detection of Unsaponifiable Oils.—The qualitative detection takes place by observing the behavior of the solution obtained by boiling the oil with alcoholic potash when diluted with warm water. Any unsaponifiable material will manifest itself as oily drops in the clear alcoholic solution, or as a whitish cloud on the addition of water.

The quantitative determination may take place in two ways: 1. From the saponification number. 2. By gravimetric methods.

1. *From the Saponification Number.*—By Table X it will be noticed that, except for Castor, Rape, and Sperm oils, the saponification number averages 193. If the number found be divided by this figure, the percentage of saponifiable matter will be obtained; this subtracted from 100 will give the unsaponifiable matter. This method gives no idea of the kind of saponifiable matter.

2. *By Gravimetric Methods.* — The procedure is essentially that of Spitz and Hönig:[1] Ten grams of the oil are boiled fifteen minutes at a return-flow condenser with fifty cubic centimeters of five per cent. alcoholic potash;[2] forty cubic centimeters of water are added and the boiling repeated. The liquid is allowed to cool, washed into a separatory

---

[1] Z. ang. Chem., **19**, 565 (1891).

[2] The potash is made by dissolving purified potash in the smallest possible quantity of water and adding absolute alcohol.

funnel with fifty per cent. alcohol and fifty cubic centimeters of 86° gasolene, thoroughly shaken and allowed to stand. The gasolene layer should separate clearly and quickly from the soap solution and the latter is drawn off; the gasolene is washed two or three times with fifty per cent. alcohol to extract any soap, and these washings added to the soap solution. This latter is extracted until upon evaporation the gasolene leaves no stain upon paper, care being taken to wash the gasolene extracts each time with fifty per cent. alcohol; three extractions with gasolene are usually sufficient.

The gasolene is distilled from these extracts, the residue heated until the gasolene odor disappears, and weighed. From the appearance of the residue some idea of the kind of unsaponifiable matter can be obtained. This in the case of sperm oil will be mainly solid alcohols, probably of the ethylene series.

According to Schicht and Halpern[1] this method is open to the following errors: incomplete saponification, incomplete extraction, solubility of soaps in the solvent, and the solubility of the unsaponifiable matter in the washing solution. Their improved method is as follows: five grams fat[2] with three grams solid caustic potash dissolved in a little water and 25 cc. absolute alcohol are boiled half an hour under a reflux condenser. After cooling 25 cc. of 10 per cent. KC1 are added and the solu-

---

[1] Chem. Ztg., 31, 279 (1907).

[2] Or 10 or 20 times this weight.

tion is then shaken four times with 200 cc. petroleum ether distilling under 60°. The petroleum ether is evaporated and, without washing, the residue is dissolved in 25 cc. absolute alcohol and the solution made slightly alkaline with normal alkali; 25 cc. of 10 per cent. KCl are added and the shaking with petroleum ether repeated. The petroleum ether solution is shaken with 100 cc. of 50 per cent. alcohol and the wash solution with 100 cc. petroleum ether, which is afterwards washed with 100 cc. of 50 per cent. alcohol. After combining the extracts the petroleum ether is driven off and the residue dried and weighed.

Notes.—Care should be taken to use gasolene which leaves no residue on evaporation at 100° C.

Identification of the Unsaponifiable Matter.—The unsaponifiable matter is either liquid or solid: in case it is liquid, it may be (1) *hydrocarbon oils,* either mineral, or formed by the distillation of waste fats, as wool grease, Chapter VIII; or (2) *tar oils,* "dead oils," etc., obtained by the distillation of coal tar; or (3) *rosin oils,* p. 126.

If it be a question of one of these three, the specific gravity will usually decide it; that of the hydrocarbon oils is 0.855 to 0.930, of the rosin oils 0.96 to 0.99, while the tar oils are heavier than water. Rosin oils would be shown by the Liebermann-Storch test, p. 127; a mixture of mineral and tar oils would be identified by treatment with an equal quantity of nitric acid, sp. gr. 1.45, both previously cooled to 15° C., and noting the rise of temperature. Mineral oils give a very slight rise, being paraffines, while the tar oils belong to the benzole series and are more easily nitrated. Hydrocarbon oils from distilled grease oleines can be identified by their refractive index and rotatory power, p. 153.

Solid unsaponifiable matters may be:

(4) *Paraffine*, p. 108.

(5) *Ceresene*—refined ozokerite.

(6) *Higher alcohols* of the paraffine series, as cetyl, $C_{16}H_{33}OH$, coming from the saponification of sperm oil and other waxes.

(7) *Cholesterol*, $C_{26}H_{43}OH$, and its isomers, phytosterol, sitosterol, isocholesterol, etc.

(8) *Lactones*, internal anhydrides of oxy acids, as stearlactone,

$$C_{14}H_{28}CHOHCH_2CH_2COOH = C_{14}H_{28}\underline{CHCH_2CH_2C}OO + H_2O.$$

These may be separated by boiling for two hours[1] with an equal quantity of acetic anhydride; if the substance dissolves and does not precipitate on cooling, higher alcohols are indicated; if a mass of crystals separates out on cooling, cholesterol and its isomers, or a mixture of these with the higher alcohols is indicated; if an oily layer remains on top, it is an indication of the presence of paraffine or ceresene. For the complete separation and identification of these reference must be had to Lewkowitsch, "Analysis of Fats, Oils, and Waxes," as it is beyond the limits of this volume.

---

[1] Wool grease may require a more prolonged treatment. See also p. 98.

SPECIAL TESTS FOR CERTAIN OILS.

Lewkowitsch[1] states that little reliance can be placed upon the color reactions of the various oils, an opinion in which the writer can cordially concur[2]; with the exception of the Bechi, Baudouin, and Halphen tests, in the majority of cases with a doubtful sample the doubt will still exist after the color test has been performed.

Bechi's Test for Cotton-seed Oil. — This depends upon the supposition that a substance of an aldehydic nature which reduces silver nitrate is contained in the oil. The method is essentially that of Milliau.[3]

Fifteen grams of oil are weighed into a No. 6 porcelain dish, using the coarse scales, and heated for about ten minutes upon the water-bath; a mixture of ten cubic centimeters of thirty per cent. caustic soda and ten cubic centimeters of the alcohol is slowly poured upon the oil. The whole is occasionally stirred until the mass becomes clear and homogeneous, and one hundred and fifty cubic centimeters of hot distilled water slowly added so as not to decompose the soap, and the boiling continued until the alcohol is expelled. Dilute sulphuric acid (1:10) is added to acid reaction, and the separated fatty acids washed three times by decantation with cold water. A portion of these is brought into a large test-tube, fifteen cubic centimeters of alcohol and two cubic centimeters of three per cent. silver

---

[1] J. Soc. Chem. Ind., 13, 617 (1894). [2] J. Ind. & Eng. Chem. 9, 136 (1917).
[3] J. Am. Chem. Soc., 15, 164 (1893).

nitrate solution are added, the tube is wrapped with brown paper, held in place by an elastic band, and heated, with constant stirring, in the water-bath until one-third of the alcohol is expelled, which is replaced by ten cubic centimeters of water. This heating is continued for a few minutes longer and the coloration of the insoluble fatty acids observed. The presence of cotton-seed oil in any appreciable proportion causes a mirror-like precipitate of metallic silver, which blackens the fatty acids of the mixture.

Notes.—The alcohol should be proved free from aldehyde by a blank test. Unless the mixture in the test-tube be thoroughly stirred while heating, it will "bump" and eject the contents. Other methods of procedure consist in applying the test to the oil itself, often after treatment with dilute caustic soda and nitric acid. (Wesson.[1]) The writer had a case in which the *oil* gave the test while the *fatty acids* gave no blackening, showing there was something in the oil itself other than cotton-seed oil which reduced the silver nitrate. Students have no difficulty in detecting a five per cent. adulteration with cotton-seed oil.

Dupont[2] thinks that the reduction of silver nitrate is due rather to sulphur compounds contained in the oil; by passing steam over the oil he obtained a product containing sulphur and the oil still gave the Bechi test. This work has been repeated and

---

[1] J. Am. Chem. Soc., **17**, 723 (1895).

[2] Bull. Soc. Chem. (3) **13**, 696; J. Soc. Chem. Ind., **14**, 811 (1895); also Charabot and March, Bull. Soc. Chim., **21**, 252 (1899).

confirmed by the author.[1] It is to be noted that while the fatty acids blacken silver nitrate they do not color cadmium, lead, or copper salts, but reduce mercury compounds. No indication of an aldehyde was noted by the fuchsine or ammonia tests. The supposition that the reducing substance is aldehydic in its nature finds support in the fact that if the oil be heated to 240°[2] or be kept for some time[3] it loses this peculiar property.

By purifying the acids by the lead salts Tortelli and Ruggeri[4] are able to detect as little as ten per cent. of heated cotton-seed oil.

Halphen's Test for Cotton-seed Oil.[5]—This depends upon the observation that this oil contains an unsaturated fatty acid which combines with sulphur, giving a colored compound.[6]

Procedure.—Ten cubic centimeters of the oil or melted fat are heated, in a large test-tube with a long glass condenser tube attached, with an equal volume of amyl alcohol and of carbon bisulphide solution of sulphur (Reagents), at first with frequent agitation, in a steam-bath, and then, after the violent boiling has ceased, in a brine bath (105°–110°) for forty-five minutes to three hours, according to the quantity of adulterant present, the tube being occasionally removed and shaken. As little

---

[1] Gill and Dennison, J. Am. Chem. Soc., **24**, 397 (1902).

[2] Holde, J. Soc. Chem. Ind., **11**, 637 (1892).

[3] Wilson, Chem. News, **59**, 99 (1889).

[4] J. Soc. Chem. Ind., **20**, 753 (1901).

[5] Halphen, J. Pharm. Chim. (1897), 390.

[6] Raikow Chem. Ztg., **24**, 562, 583 (1900).

as one per cent. will give a crimson wine coloration in twenty minutes.[1]

Notes.—If the mixture be heated for too long a time a misleading brownish-red color due to burning is produced. The reaction seems to be peculiar to this oil; it is more sensitive with fresh than old fats, and while, by comparison with a blank, one-sixteenth of one per cent. is noticeable, one-fourth of one per cent. is easily detected. Cotton-seed oil which has been heated to 250° does not give the test; the oil is then not available as food. Heating to 200° does not interfere with the test.[2,3]

The test is not given by an oil which has been oxidized with sulphuric acid and potassium permanganate, although such an oil gives the Bechi test.[4] This shows that the two tests are not produced by the same substance. Nor is this test or that of Bechi given by an oil which has been treated with chlorine or sulphurous acid.[5] If treated with the former it is no longer edible; an oil treated with sulphurous acid and washed with alcohol cannot be distinguished from ordinary cotton-seed oil and does not, as already stated, respond to either the Halphen or Bechi test. In this case the test for phytosterol is the only means of determining if it has been added to an animal oil.

---

[1] Oilar, Am. Chem. J., **24,** 355; abstr. Anal., **26,** 22 (1901).

[2] Fischer and Peyan, Analyst, **30,** 131 (1905).

[3] Soltsien, Z. öffentl. Chem., **5,** 135 (1899); J. Soc. Chem. Ind., **18,** 865.

[4] Raikow, loc. cit.

[5] Petkow, Analyst, **32,** 123 (1907).

Lard from hogs fed on cotton-seed meal shows this reaction strongly, as if it were twenty-five per cent. oil.[1] The butter from cows similarly fed also yields the reaction.[2]

The test may be applied to the soaps or fatty acids, provided they are not too deeply colored.

The amyl alcohol cannot be omitted nor substituted by ethyl alcohol without impairing the delicacy of the test.[3] The compound in the oil cannot be removed by treatment with animal charcoal.[4]

Baudouin's, or really **Camoin's, test for Sesame Oil.**—Villavecchia and Fabris[5] apply the test as follows: 0.1 gram sugar is dissolved in ten cubic centimeters of hydrochloric acid of specific gravity 1.18 in a test-tube and twenty grams of the oil to be tested added, the whole thoroughly shaken and allowed to stand. In the presence of one per cent. of sesame oil the aqueous liquid will be colored red,[6] due to the action of the furfurol formed upon the oil. They state that as olive oils of undoubted purity have shown the reaction in the aqueous layer and not in the oily stratum, the color should be looked for in the latter.

The sugar may be replaced by 0.1 cubic centimeter of a two per cent. solution of furfurol and half the quantity of oil used.

---

[1] Soltsien, Z. öffentl. Chem., **7**, 140 (1901).

[2] Wauters, J. Soc. Chem. Ind., **19**, 172 (1900).

[3] Soltsien, loc. cit., **25**, Oilar, loc. cit.

[4] Utz, Rev. Fett.-Harz.-Ind., **9**, 125 (1902).

[5] Z. angew. Chem., 509 (1892); abstr. J. Soc. Chem. Ind., **12**, 67; also Kerp, Analyst, **24**, 246 (1899).

[6] Ibid. (1893), 505; abstr. Analyst, **19**, 47.

Milliau[1] saponifies as in the Bechi test and dries the acids at 105°. Lewkowitsch[2] states that this is a needless complication. Da Silva[3] states that this test has given colors with certain Portuguese olive oils. Kreis[4] states that the active or color-giving constituent is probably phenolic in its nature. The reaction is given by other substances,[5] as vanillin, oil of cloves, and cinnamon; this should be borne in mind in testing oils which have been extracted from confectionery. Rancid fats prevent the coloration; it can, however, be brought about even in rancid fats by the addition of an equal quantity of cotton-seed oil.[6]

Bach's Test.—According to O. Bach,[7] the acids obtained from rape-seed oil are completely insoluble in David's alcoholic acetic acid, in the proportion of one to fifteen, by volume; those from cottonseed, peanut, sesame, and sunflower oil dissolve on heating. Those from the last oil separate as a granular precipitate at 15°, while from the other three they gelatinize. The acids from olive oil are completely soluble at the ordinary temperature. David's acid is made by mixing twenty-two cubic centimeters of fifty per cent. acetic acid (by volume) with thirty cubic centimeters of alcohol, sp. gr. 0.817, 92.07 per cent. (by weight).

---

[1] J. Am. Chem. Soc., **15**, 162 (1893).

[2] "Oils, Fats, and Waxes."

[3] J. Soc. Chem. Ind., **17**, 275 (1898).

[4] Chem. Ztg., **27**, 316 (1903).

[5] Gerber, Analyst, **32**, 90, (1907).

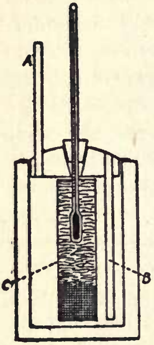
[6] Lauff and Hinsmann, Chem. Ztg., **31**, 1023 (1908).

[7] Allen, "Commercial Organic Analysis," vol. ii., pt. 1, p. 128 (1899).

Notes.—The author has found that Bach's observation cannot be implicitly relied upon, as some rape-seed oils yield acids which are soluble in David's mixture.

Free Acid Test.—About ten grams of oil are weighed (to centigrams) into a 250 cubic centimeter Erlenmeyer flask, sixty cubic centimeters of neutral alcohol (Reagents) added, the mixture warmed to about 60° C., and titrated with $\frac{N}{6}$ potassium hydrate, using phenolphthalein, the flask being frequently and thoroughly shaken. The result is conventionally reported in per cent. of oleic acid[1]; 1.0 cubic centimeter $\frac{N}{6}$ KOH is equivalent to 0.047 gram oleic acid.

FIG. 9.



Mackey's apparatus.

Spontaneous Combustion Test.—*Mackey's Apparatus.*—The apparatus,[2,3] Fig. 9, consists of a cylindrical copper water-bath 7 inches high and 4 inches in diameter (inside measurements), surrounded with a half-inch water-jacket. The cover is packed with asbestos and carries the draft tubes A and B, ½ inch in diameter and 6 inches long, which cause a current of air to be sucked down B and up A, thus ensuring a circulation of air in the apparatus: C is a cylinder made of 24-mesh wire gauze 6 inches high and 1½ inches in diameter

---

[1] Or in mgms. KOH per gram of oil.

[2] Mackey, J. Soc. Chem. Ind., **15**, 90 (1896).

[3] Gill, Id., **26**, 185 (1907).

and supported upon a projection from the bottom of the bath. A thermometer projects down into the center of the cylinder; if a metal condenser be connected to the water-bath it can be used indefinitely without refilling and without danger of burning out.

Seven grams of ordinary bleached cotton wadding are weighed out in a porcelain dish or on a watch-glass, and 14 grams of the oil to be tested poured upon the cotton and thoroughly worked into it, care being taken to replace any oil that is lost. The cotton is then placed in the cylinder, packed about the thermometer so that it occupies the upper 4½ inches of the cylinder, and put into the boiling water-bath. After the expiration of an hour, the bath having been kept in active ebullition, the temperature is read. Any oil which shows a temperature exceeding 100° C. in one hour or 200° C. in two hours should be regarded as a dangerous oil, or liable to produce spontaneous combustion. The following tables show the results obtained in using this apparatus.

	Temperature °C. in		
Oil	1 hr.	1¼ hrs.	1½ hrs.
Olive (neutral)	97–98	100	101
Cotton-seed	112–128	177–242	194–282
Elaine	98–103	101–115	102–191
Olive fatty acids	102–114	....	196

Other values obtained were:

Oil	Temp. °C.	Time Minutes	Iodine No.	Free Acid per cent.
Olive	234	130	85.4	5.3
Lard	234	75	75.2	Trace
Oleic Acid	158	188	60.5	....
Cotton-seed	234	70	108.9	Neutral
Linseed	234	65	168.1	Neutral
25° Paraffin	97	135	16.2	....

Besides being used for testing oils it can be applied to testing other materials, oily waste, sawdust, or any mixture suspected of causing spontaneous combustion.

Other apparatus, particularly that of Ordway,[1] described in earlier editions of this book, while giving trustworthy results, has not been found to give such rapid and concordant results as are obtained with Mackey's.

For an account of early experiments along this line reference may be had to papers by Coleman and Dollfus in the Bulletin of the Industrial Society of Mulhouse, 1875 and 1876.

"The results[1] of the greatest practical value obtained in the use of this apparatus have been, first, determining the cause of fires; and, second, determining the degree of safety of the various oils used in manufacturing. Mineral oil, as is well known, is not liable to spontaneous combustion; and a certain percentage of animal or vegetable oil may be added to mineral oil without materially increasing the danger under ordinary circumstances. This percentage varies according to the oil; with neat's-foot and first quality lard oil some fifty to sixty per cent. may be used, with cotton-seed not over twenty-five per cent. is allowable. The claim so often made for so-called 'safe' oils, said to have been changed by special and secret processes of refining so as to be no longer dangerous, is easily exposed by this test."

---

[1] **Richards, Tech. Quarterly, 4, 346 (1891).**

Drying Test.—This is, as would be implied, more especially applicable to the drying oils; there are two ways of applying it, exposure of the oil upon finely divided lead (Livache test) and upon a plate of glass.

Livache Test.[1]—One gram of precipitated lead is spread out in a thin layer on a three-inch flat watch-glass and accurately weighed; 0.5 to 0.6 gram of the oil (twenty to twenty-four drops) are brought upon the lead from a pipette, taking care that the drops do not touch each other, the watch-glass and contents again accurately weighed, and exposed to light and air at ordinary temperature. It is weighed from time to time, the maximum weight being reached in from eighteen to seventy-two hours. The oil that increases most in a given time is considered to be the best drying oil.

Lippert[2] confirms Weger's opinion that the Livache test as here carried out is unreliable and advises the use of copper powder instead of lead. This is known as "cement copper," and is prepared similarly to the precipitated lead.

Test upon Glass.[3]—A few drops of the oil are brought upon a glass plate inclined at about thirty degrees from the horizontal. A test of the oil is made from time to time by touching it with the fingers, the time at which it does not soil them being noted as the point when it is dry. Good oil should dry in three days.

---

[1] Compt. rend., **102**, 1167 (1886).

[2] Rev. Fett.-Harz.-Ind., **6**, 65; abstr. J. Soc. Chem. Ind., **18**, 693 (1899).

[3] Amsel, J. Soc. Chem. Ind., **15**, 222 (1896).

Archbutt[1] makes this test as follows: A piece of polished plate-glass seven centimeters square by four millimeters thick is cleaned and counterpoised on the balance; it is then heated for an hour at 200° C. in an air-bath to thoroughly dry it. It is taken out, laid on a non-conductor, allowed to cool for three or four minutes, and the hot glass thinly painted with the oil to be tested by means of a camel's-hair brush. When the glass is cold it is weighed and sufficient oil added to make it up to 0.1 gram. Two glasses are coated with the sample and two with a standard oil, all placed on a level surface in a large air-bath at 50° C. and heated for nine hours; one set of plates is withdrawn, cooled, and tested by the finger. Good raw linseed is tacky, when tested by the finger when cold, in nine hours and dry in twelve; corn oil is practically dry in fifteen hours, though slightly tacky; cottonseed, partially dry in eighteen hours and fully dry in twenty-one. Refined rape oil dried in forty-eight hours, and olive oil was sticky after thirteen days.

Titer Test.—Under this rather misleading title is expressed the solidification point of the fatty acids derived from a fat or oil; it has nothing at all to do with titration, as might be expected. The test is extensively used for the evaluation of fats, and according to the method provisionally adopted by the Association of Official Agricultural Chemists is carried out as follows:[2]

---

[1] J. Soc. Chem. Ind., **18**, 347 (1899).

[2] U. S. Dept. of Agriculture, Bureau of Chemistry Bulletin No. 107, p. 135 (1907).

(a) Standard Thermometer.

The thermometer must be graduated in tenth degrees from 10° to 60°, with a zero mark, and have an auxiliary reservoir at the upper end, also one between the zero mark and the 10° mark. The cavity in the capillary tube between the zero mark and the 10° mark must be at least 1 cm. below the 10° mark, the 10° mark to be about 3 or 4 cm. above the bulb, the length of the thermometer being about 15 inches over all. The thermometer is annealed for 75 hours at 450° C., and the bulb is of Jena normal 16''' glass, moderately thin, so that the thermometer will be quick acting. The bulb is about 3 cm. long and 6 mm. in diameter. The stem of the thermometer is 6 mm. in diameter and made of the best thermometer tubing, with scale etched on the stem, the graduation to be clear-cut and distinct, but quite fine.

(b) Determination.

Saponify 75 grams of fat in a metal dish with 60 cc. of 30 per cent. sodium hydroxid (36° Baumé) and 75 cc. of 95 per cent. (by volume) alcohol or 120 cc. of water. Boil to dryness, with constant stirring to prevent scorching, over a very low flame or over an iron or asbestos plate. Dissolve the dry soap in a liter of boiling water, and if alcohol has been used, boil for forty minutes in order to remove it, adding sufficient water to replace that lost in boiling. Add 100 cc. of 30 per cent. sulphuric acid

(25° Baumé) to free the fatty acids, and boil until they form a clear, transparent layer. Wash with boiling water until free from sulphuric acid, collect in a small beaker, and place on the steam bath until the water has settled and the fatty acids are clear; then decant them into a dry beaker, filter, using the hot-water funnel, and dry twenty minutes at 100° C. When dried, cool the fatty acids to 15° or 20° C. above the expected titer and transfer to the titer tube, which is 25 mm. in diameter and 100 mm. in length (1 by 4 inches) and made of glass about 1 mm. in thickness. Place in a 16-ounce saltmouth bottle of clear glass, about 70 mm. in diameter and 150 mm. high (2.8 by 6 inches), fitted with a cork, which is perforated so as to hold the tube rigidly when in position. Suspend the thermometer, graduated to 0.1° C., so that it can be used as a stirrer, and stir the mass slowly until the mercury remains stationary for thirty seconds. Then allow the thermometer to hang quietly, with the bulb in the center of the mass, and observe the rise of the mercury. The highest point to which it rises is recorded as the titer of the fatty acids.

Test the fatty acids for complete saponification as follows:

Place 3 cc. in a test-tube and add 15 cc. of alcohol (95 per cent. by volume). Bring the mixture to a boil and add an equal volume of ammonium hydroxid (0.96 sp. gr.). A clear solution should result, turbidity indicating unsaponified fat. The titer must be made at about 20° C. for all fats having a titer above 30° C. and at 10° C. below the titer for all other fats.

REFERENCES.

Hefter, G. Technologie der Fette, Oele, und Wachsarten des Pflanzen und Tierreichs. 4 volumes, 1906+

Ubbelohde, L. Chemie, Analyse und Gewinnung der Oele, Fette und Wachse. 4 volumes, 1908+

CHAPTER IV.

GENERAL CONSIDERATIONS REGARDING LUBRICANTS.

Method of Examination of an Unknown Oil.

According to the results of the viscosity and friction tests, the least viscous oil is to be given the preference. It should be borne in mind, however, that the heat of the journal diminishes the viscosity: for example, at 60° F., if the viscosity of sperm oil be taken as 100, that of 25° paraffine oil is 123; at 100° F. the latter has diminished to 110, and at 250° F. they are practically equal. On account of this change in temperature, as well as the irregularities of the journals, of the feed, and of pressure, a too thinly fluid oil must not be chosen.

The following considerations will aid in the selection of a suitable oil.

1. The flashing point of the oil should be above 300° F.

2. The oil should have an evaporation test of less than five per cent.

3. On general principles the most fluid oil that will stay in place should be used.

4. The best oil is that which possesses the greatest adhesion and least cohesion. This condition is fulfilled, first, by fine Mineral Oils;[1] second, Sperm; third, Neat's-foot; fourth, Lard.

---

[1] Except at high temperatures. Doolittle, J. Am. Chem. Soc., **20**, 238 (1898).

5. For light pressures and high speeds, Mineral Oils of specific gravity 30.5° Bé., flash point 360° F., Sperm, Olive, and Rape (Thurston adds also Cotton-seed), should be employed.

6. For ordinary machinery, Mineral Oils of specific gravity 25° to 29° Bé., flash point 400° to 450° F., Lard, Whale, Neat's-foot, and Tallow, also heavy Vegetable Oils, should be used.

7. For cylinder oils, Mineral Oils of specific gravity 27° Bé., flash point 550° F., alone and with small percentages (1 to 7) of Animal or Vegetable Oils, are employed; the latter are Degras, Tallow, Linseed, Cotton-seed, and blown Rape.

Note.—The above specifications apply to oils of paraffine base; the asphaltic base oils are about 7° Baumé heavier, flash lower and are much more viscous than the corresponding paraffine base oils; they also lose their viscosity more rapidly except at high temperatures, when the reverse holds true. Consequently when these oils are specified, their viscosity should be from 25 to 50, or in some cases, even 75 per cent. greater.

8. For watches and clocks, clarified Sperm, Jaw, and "Melon" oils should be employed.

9. For heavy pressure and slow speed, Lard, Tallow, and other greases, either by themselves or mixed with Graphite and Soapstone, should be used.

10. For very heavy pressure, solid lubricants, as Graphite and Soapstone, are employed.

11. To resist cold, as, for example, for lubricating air-driven rock-drills, Kerosene has been used.

12. The oil should contain no acid to corrode the shaft or journal; the German railroads[1] permit no more than 0.1 to 0.3 per cent. of acids, calculated as sulphuric anhydride, in their oils. For the action of oils upon metals reference may be had to Table XII.

In addition to the conditions outlined in considerations 1–12, reference should be had to pp. 160–171, the way and manner in which the oil is applied, or the "feed," influences the choice. The various feeds may be divided into Forced, Gravity, Ring or Wick, Splash, Flooded bearing and Hand feed, or combinations of these. Of these the forced, gravity, and ring or wick, are economical, of high efficiency, collect little dirt, and in the case of the first two, furnish strained oil and use a light or medium-bodied oil; the same holds true of the flooded bearing, except as regards the efficiency of the recovery of the oil. The chief disadvantage of the splash feed, is that any dirt and wear from the bearings are not separated from the oil. Hand feeding is most wasteful and inefficient, depending upon the efficiency of the individual. Forced feed is employed with high speed and bearing pressures; it uses a somewhat more viscous oil—particularly with automobiles, than the other types of feed.

Wear and Tear of Oils.—The question is often asked as to whether oils "wear out"; this continues the Southwick conception of the ball bearing and

---

[1] Aisinmann, Z. angew. Chemie, **11**, 213: abstr. J. Soc. Chem. Ind., **14**, 811 (1895).

implies that the balls or molecules break or wear out. Carpenter and Sawdon showed that the gravity and viscosity of the oils in circulating systems increased, but the actual friction test was slightly lower at low pressures, and a trifle higher at high pressures. With automobile lubrication, the dilution of the oil by the gasoline residues causes it to become thinner; consequently fresh oil should be added to a circulating system to keep this viscosity practically constant.

DENTON, Trans., A. S. M. E., **9**, 369 (1888); **11**, 1013 (1890).
ARCHBUTT and DEELEY, "Lubrication and Lubricants," 48-131.
WM. M. DAVIS, "Friction and Lubrication."
HOLDE-MUELLER, "Examination of Hydrocarbon Oils."
BATTLE, "Industrial Oil Engineering," 1920.
THOMSEN, "The Practice of Lubrication," 1920.
HAMOR & PADGETT, "The Examination of Petroleum Products," 1920.

Method of Examination of an Unknown Oil.

There being no specific tests for the different oils,[1] as in the case of the various elementary substances, the analyst should, in attacking an unknown oil, ascertain all possible facts about it, as the source, the use to which it is put, and the cost. A low-priced oil is not likely to be adulterated with one of higher cost. While the prices fluctuate to a considerable extent, yet the following table, it is believed, represents the average price of the various oils, the highest price being given first:

---

[1] At the present state of our knowledge (1921) we can detect the following oils with certainty: Castor, Cokernut, Cotton-seed, Peanut, Rosin, and Sesame. We can be reasonably certain of 25 per cent. of Corn, Rape, and Sperm oils.

1. Almond.
2. Castor.
3. Sesame.
4. Neat's-foot.
5. Rape.
6. Olive.
7. Sperm.
8. Whale.
9. Peanut.
10. Linseed.
11. Tallow.
12. Lard.
13. Cod.
14. Cotton-seed.
15. Mineral.
16. Rosin.

Certain physical properties may aid in the examination. The *color* is of little assistance, as oils may be colored by the use of the oleates or butyrates of iron or copper. *Fluorescence* is valuable as indicating the presence of mineral oil; this can be shown by placing a few drops of the oil on a sheet of ebonite and observing the bluish color.

The *odor* and *taste*, as has already been stated, may to experts reveal much about the nature of the oil under examination. Marine animal oils are detected, especially when warm, by their strong "fishy" odor, while neat's-foot, tallow, lard, olive, rosin, and linseed oils each have a well-marked and easily distinguishable odor. Whale oil has a nutty, and rape oil a harsh, unpleasant taste.

The *specific gravity* should next be noted, the oil being exactly at 15° C. The accompanying table shows the groups into which the oils are divided by this criterion:

.875–.884.	.884–.912.	912.–.920.	.920–.937.	.937–.970.
Sperm.	Oleic Acid.	Almond. Lard. Neat's-foot. Olive. Peanut. Rape. Tallow.	Corn. Cotton-seed. Fish. Linseed. Poppy-seed. Sesame.	Castor. Blown Oils. Chinese Wood.

The *elaidin* test (page 55) may be applied next, to allow time for the cake to form; it will be followed by the Valenta (page 54) and Maumené (page 56) tests, all of these being done in duplicate. In making the elaidin test, it is advisable to carry on an experiment under the same conditions with a known sample of lard oil.

From the result of the examination up to this time a reasonably good idea of the nature of the oil will have been obtained; the *iodine* test can now be applied and the percentage of adulteration approximated. The data obtained by the Maumené test and specific gravity determination will serve as checks upon this. In case Sesame, Cotton-seed, Peanut, or Rosin oils be suspected, the specific tests for them can be made.

The *saponification* test, unless mineral oil be suspected, need rarely be resorted to; the reason being that it would show practically nothing regarding the nature of the oil. This is evident from Table X. Of all the oils there given, this constant, excepting Castor (181), Rape (174), and Sperm (135), being about 193. Finally, where the importance of the case will warrant, the analyst is advised to prepare a mixture of the oils, using the proportions indicated by the various tests, and subject it to the more rapid tests, as the Specific Gravity, Viscosity, Maumené, and Bromine Number. It should be borne in mind in making out the report[1]

---

[1] Results except in rare cases cannot be reported more closely than 0.5 per cent.

that, excepting in the case of the special tests, the results of *one* test cannot be relied upon to determine the nature of an oil, but the evidence of all the tests here given should be carefully weighed and compared before rendering a final verdict.

Test for Animal or Vegetable Oils.—Animal oils contain cholesterol, $C_{26}H_{43}OH$, while vegetable oils contain the isomeric body phytosterol; hence the isolation and identification of these compounds enables one to say with certainty as to the presence of one class of oil or the other—for example as to the presence of fish oil in linseed. The quantity of these bodies varies from 0.2 to one per cent. The method is essentially that of Bömer.[1,2,3] Fifty grams of the oil are boiled in a flask with a return cooler with 75 cc. of 95 per cent. alcohol for five minutes and the alcoholic solution separated; this is repeated with another portion of alcohol. The alcoholic solutions are mixed with 15 cc. of 30 per cent. sodium hydroxide and evaporated on a water-bath nearly to dryness in a porcelain dish and the residue shaken out with ether. The ether is evaporated, the residue taken up with a little ether, filtered, again evaporated, dissolved in 95 per cent. alcohol (by volume), and allowed to crystallize slowly. Bömer states that the form of the crystals is more to be relied upon than a determination of their melting point. Cholesterol crystallizes from

---

[1] J. Soc. Chem. Ind., **17**, 954 (1898).
[2] Tolman, J. Am. Chem. Soc., **27**, 590 (1905).
[3] Tolman, Bull. 107, U. S. Dept. Agriculture (1907).

alcohol or ether in leaflets or rhomboid tables containing one molecule of water of crystallization. Phytosterol crystallizes also from alcohol with one molecule of water in needles forming stars or bundles. As a further means of identification, some of the esters should be made and their melting points determined.

To this end the crystals above obtained are heated over a low flame in a small porcelain dish covered with a watch-glass, with 2 or 3 cc. of acetic or other acid anhydride until it boils: the watch-glass is removed and the excess of anhydride evaporated on the water-bath. The contents of the dish are treated with a small quantity of absolute alcohol to prevent crystallization, more alcohol added and the solution allowed to crystallize. The crystals are filtered off through a very small filter, washed with a small quantity of 95 per cent. alcohol, dissolved in absolute alcohol, and recrystallized until a constant melting point is obtained.

The following table shows the corrected melting points of these alcohols and their esters:

	Cholesterol.	Phytosterol.
Alcohol	148–150.8°	136–143.8°
Acetate	113–114°	120–137°
Benzoate	145–151°	142–148°
Propionate	97–98°	104–105°

Notes.—Some directions state, in isolating the cholesterol or phytosterol, to boil with the 30 per cent. sodium hydroxide until one-fourth of the alcohol is evaporated. As a result of repeated experiments this has been found to cut down the yield so much that on a large scale practically none of these bodies, particularly phytosterol, was obtained. This agrees with the observation of Lewkowitsch that by heating cholesterol with normal alcoholic potash, cholesterin hydrate is obtained.

The following test will serve to differentiate between cholesterol and phytosterol.[1,2] A very small quantity of cholesterol is warmed with 1.5 cc. absolute alcohol and a trace of isodulcit or rhamnose (δ-dimethylfurfural) added. After cooling, an equal volume of concentrated sulphuric acid is added, so as to form a layer below the solution, whereupon a raspberry-colored ring is produced at the zone of contact of the two liquids. On mixing the layers while the tube is cooled in a current of cold water, the mixture becomes intensely colored. With phytosterol the reaction fails or at most a pink color. Similar reactions are given by abietic acid.

As little as one per cent. of cotton-seed has been found in lard, and four per cent. in any oil have been detected by this test.

Another method is as follows: to a small portion of the sterol obtained from the oil in question add an equal quantity of pure phytosterol or cholesterol and determine the melting point of the mixture. If this remains unchanged the sterol is phytosterol or cholesterol.

---

[1] Neuberg and Rauchwerger, abstr. J. Soc. Chem. Ind., **23**, 1163 (1904.)

[2] Lewkowitsch states that the digitonin method has not always yielded satisfactory results.

[3] Arbeit. a. d. K. Gesundheitsamte, **22**, 576 (1905).

Polenske[3] has found that a small quantity of paraffine influences the melting point of the sterol acetates. It should therefore be removed from the crude unsaponifiable matter by treating it (0.1 gm.) with 1 cc. of petroleum ether (Bpt. below 50°) for at least 20 minutes at 15° C. It is transferred to a filter of cotton and washed with five successive portions of 0.5 cc. each. The paraffine is readily removed and the cholesterol is more soluble than the phytosterol.

For the means of distinguishing between drying and marine animal oils, see Halphen, J. Pharm. Chim., **14**, 391 (1901), abstracted J. Soc. Chem. Ind., **21**; 74, or Chem. Centralb., **72**, ii., 1097 and 1323.

PART II.

DERIVATION, DESCRIPTION, AND EXAMINATION.

DERIVATION, DESCRIPTION, AND EXAMINATION OF CERTAIN OILS.

In this part the technology and properties of the more commonly occurring oils will be considered under the following heads:

1. Source and Preparation.
2. Physical Characteristics.
3. Chemical Composition.
4. Analytical Constants.
5. Adulterations and their Effects.
6. Uses.

The analytical data are the average of the results from many sources; in addition to these the highest and lowest results are often given.

The classification of the animal and vegetable oils is that of Lewkowitsch, following in the various groups of oils the order of the iodine values.

A. Oils and Fats. Glycerides.

1. VEGETABLE OILS.
    (1) Drying Oils.
    (2) Semi-drying Oils.
    (3) Non-drying Oils.

2. ANIMAL OILS.
  (1) *Marine Animal Oils.*
    α. Fish Oils.
    β. Liver Oils.
    γ. Blubber Oils.
  (2) *Terrestrial Animal Oils.*

B. Waxes. Non-Glycerides.

LIQUID WAXES.

CHAPTER V.

PETROLEUM PRODUCTS.

CRUDE petroleum varies so much with the locality that any statement about it is only approximate; according to Peckham,[1] the products which may be obtained from Pennsylvania petroleum are about as follows:

First. The NAPHTHA DISTILLATE, all that passing over above 60° Baumé, about sixteen and five-tenths per cent.

Second. The BURNING OIL DISTILLATE, that passing over between 60° and 36° Bé., about fifty-four per cent.

Third. The LUBRICATING OIL DISTILLATE, that passing over from 36° to 23° Bé., about seventeen and five-tenths per cent.

Fourth. PARAFFINE, two per cent.

Fifth. COKE AND LOSSES, ten per cent.

The Naphtha Distillate.—This is fractionated as follows:

I. Crude Gasolene, cut at 80° Bé., one and five-tenths per cent.

II. C Naphtha, between 80° and 68° Bé., ten per cent.

III. B Naphtha, between 68° and 64° Bé., two to two and five-tenths per cent.

---

[1] S. F. Peckham, 'Report on Petroleum," p. 165; also J. Soc. Chem. Ind., **13**, 794 (1894).

IV. A Naphtha, between 64° and 60° Bé., two to two and five-tenths per cent.

Fraction I. is redistilled and the products caught in a mixture of ice and salt, giving:[1]

1. *Cymogene,* 110° to 100° Bé., Bpt. 32° F., largely butane, used for ice-machines.

2. *Rhigolene,* 100° to 90° Bé., Bpt. 65° F., largely pentane, used as a local anæsthetic.

3. *Petroleum Ether,* Sherwood Oil, "Gasolene," 90° to 80° Bé., Bpt. 100° to 150° F., largely hexane, used for carburetting air in the various "gas-machines" and in the laboratory for oil and fat extraction.

4. *Gasolene,* Canadol, 80° to 75° Bé., Bpt. 150° to 190° F., used for oil extraction on the large scale.

Fraction II. is treated with four ounces of oil of vitriol to the gallon in an agitator with mechanical paddles, washed with caustic soda solution, and distilled with steam, yielding:

5. *Naphtha,* Danforth's Oil, 76° to 70° Bé., Bpt. 160° to 210° F., used in street lamps, stoves, torches, and gasolene engines.

Fractions III. and IV. are treated similarly to II., giving:

6. *Ligroine,* 67° to 62° Bé., Bpt. 160° to 225° F.,[2] used in pharmacy, in the laboratory, and in sponge lamps.

7. *Motor Gasoline,* 62° to 60° Bé., Bpt. 160°–320° F. For automobiles and gasoline motors.

---

[1] Sadtler, "Industrial Organic Chemistry" (1895), p. 30.

[2] Freezing point, —147° C. Cabot, J. Soc. Chem. Ind., 26, 813 (1907).

8. *Benzine* (deodorized), *V. M. and P. Naptha*, 62° to 57° Bé., Bpt. 225° to 300° F., used as a substitute for turpentine, for cleaning type, and by dyers and scourers.

The Burning Oil Distillate.—This is fractionated into:

V. Crude Burning Oil, 58° to 40° Bé., forty-two per cent.

VI. "B" Oil, 40° to 36° Bé., seventeen per cent.

Fraction V. is treated with acid similarly to II., washed, and distilled as long as the color is good. Three fractions may be obtained.

8. "Export Oil," 110° F., Fire Test (F. T.), shipped to China and Japan.

9. *Export Oil*, 120° F., F. T., shipped to England.

10. *Headlight Oil*, 150° F., F. T., 50° to 47° Bé., ordinary kerosene.

Fraction VI. is treated similarly to V., and on distillation yields:

11. *Mineral Sperm*, or Lantern Oil, 36° Bé., 250° F., Flash point, and 300° F., F. T., used for passenger traffic illumination and in light-houses.

The Lubricating Oil Distillate.—The residues from the burning oil distillate are distilled with superheated steam, various fractions being obtained; these are treated with acid, washed, and redistilled, yielding:

"Neutral" Oils, 38° to 32° Bé., used as "wool oils."

Spindle Oils, 32° to 28° Bé.

Loom Oils, 29° to 27° Bé.

Engine Oils, 27° to 23° Bé.

Cylinder Oils, 28° to 25° Bé.

These fractions are filtered through sawdust and salt to remove water, and when too deeply colored through fuller's earth or bone charcoal, after the manner of sugar syrups. There seems to be a clearly defined impression that the loss of color is also accompanied by a loss in lubricating value. Acid-treated oils emulsify more readily with water, and partly on account of the "sulpho" compounds which they contain, are less desirable as lubricants.

In addition to these distilled oils, there is another class, the paraffine oils, which are obtained by chilling and pressing certain distillates, yielding solid paraffine and paraffine oil.

Various samples of 25° Paraffine gave the following average figures:

Sp. Gr	Flash, °F.	Fire, °F.	Viscosity 70 °F.
.900	410	475	175–200
		Iodine	
		10–14	

REFERENCES.

Bacon and Hamor, The American Petroleum Industry (2 vols.), 1916.

Rogers and Aubert, "Industrial Chemistry," Chapter 23.

Battle, "Industrial Oil Engineering," 1920.

Westcott, "Handbook of Casing-head Gas(olene)," 1916.

Burrell, "Gasoline," 1916.

Stratford, "Veedol," 1916.

A. OILS AND FATS. GLYCERIDES.

CHAPTER VI.

VEGETABLE OILS.

(1) Drying Oils.

Linseed Oil.—Percentage of oil in seeds 38 to 40.

Preparation.—Linseed oil is prepared from the seeds of the flax-plant by expression or extraction. The oil receives its name according to the locality where the seed is grown. Calcutta, La Plata, and Western are some of the brands in this market; the first being considered to be the best, although sometimes equalled by the last.

Properties.—It is of a golden-yellow color and high specific gravity, the highest of any fatty oil likely to be used as an adulterant. On exposure to the air it absorbs oxygen—often causing spontaneous combustion—and dries to a gummy, insoluble substance, linoxyn.

Composition.—It contains the glycerides of isolinolenic, linolenic, linolic,[1] oleic, stearic, and palmitic acids.

CHARACTERISTICS.

Sp. Gr. 15.5° C.	Maumené.	Elaidin.	Iodine.[2]	Saponification.
.9315–.9371	103°–126° C.	Liquid	170–193	187.6–195.2
		Free Acid.		
.937–.945. (N. American seed)		8.	178[3]	189. –195[4]

---

[1] Hazura and Grüssner, Monatsh., 9, 180 (1888).

[2] Obtained by Hübl's method; this is true of this characteristic throughout the book. For differences from the other methods see table XV.

[3] Hanus method. [4] Standards Am. Soc. Test. Mat., (1918) 573. Unsaponifiable matter 1.5 per cent.

Adulterants.—Corn, Cotton-seed, Fish, and Rosin oils.

All these adulterants lower the characteristics given and diminish its drying power; *Cotton-seed* oil would be shown by the Bechi test (page 76); *Rosin* oil by the low Saponification Value, it being unsaponifiable, by the Liebermann-Storch reaction (page 127), and by the rotary power. *Fish* oil, usually menhaden oil, p. 140, may, if present in large quantity, be detected by its odor when warmed. For the detection of smaller quantities, and particularly of the deodorized oil, resort must be had to the isolation of phytosterol and cholesterol (p. 92). These should be converted into the acetates by boiling with acetic anhydride, recrystallized from absolute alcohol four or five times or until a constant melting point is obtained. Bömer and Winter state that the melting point of the phytosterol acetate crystals from pure linseed oil is 128°–129°, and that if cholesterol be present a much lower melting point is obtained.

Uses.—For preparation of paints[1] and as "boiled" and "bleached oil" for preparation of varnishes; by treatment with sulphur chloride for manufacture of rubber substitutes; and for soft soaps.

"*Boiled Oil.*"—By heating the oil—preferably in a steam jacketed kettle—from 130° C. upward, with or without the addition of litharge, red lead, lead acetate, manganese dioxide or borate, the oil becomes

---

[1] For the effect of pigments on oil see Boughton, Bur. Stand. Tech. Paper, No. 71 (1916).

oxidized, changes color, and dries much more rapidly.

The characteristics of boiled oil are as follows:[1]

Sp. Gr.15.5° C	Free Acid	Iodine (Hanus)	Saponification
.937–.945	8.0	178 (min.)	189–195

Bleached Oil.—This is an oil prepared, by special processes kept jealously guarded, for the use of varnish-makers. It may be prepared by heating linseed oil hotter than in the preparation of "boiled oil," to 260° to 300° C., or by forcing oxygen through the oil.

CHARACTERISTICS.[2]

Sp. Gr. 15° C.	Maumené.	Iodine.	Valenta.
.932–.934.	104° C.	160	60° C.

Mastbaum[3] states that pressed linseed oil has a higher iodine value than extracted because the more fluid portion is pressed out, and further, that the iodine value changes with the age of the oil.

Linseed oil for varnish-making and other refined purposes should separate but a small quantity of mucilage when heated to 300° C. The oil should be very rapidly heated to this temperature in a metal vessel, poured into a test-tube, and allowed to cool. A suitable oil shows little or no deposit, whereas a bad one may separate an amount equal in volume to the oil used.

Hexabromide Test.—This is of great value to determine the purity of a linseed oil. If the yield of hexabromides from a linseed oil is less than twenty per cent., foreign oil is present; fatty acids from genuine linseed oils yield usually from thirty[1]

---

[1] "Standards" A. S. T. M. (1916) 500.

[2] Gill and Lamb, J. Am. Chem. Soc., **21,** 29 (1899).

[3] Z. angew. Chem., **23,** 719 (1897).

to forty-two per cent. of bromides. The bromides of these acids melt at 175°–180° to a *clear liquid,* while those obtained from fish, liver, and blubber oils do not melt even at 200° and change into a dark mass. The test is best performed according to the method of Bailey & Baldsiefen, Appendix, p. 215. Where a centrifuge is not available the process of Hehner and Mitchell[1]: is used as follows:—One or two grams of the oil (0.3 gr. fatty acids) are dissolved in 40 cc. of ether to which a few cubic centimeters of acetic acid have been added. The solution is cooled to 5° and bromine added drop by drop (keeping the flask cool) until the color of bromine persists. The mixture is allowed to stand three hours to ensure complete absorption of the bromine, filtered through a weighed asbestos filter, and the precipitate washed successively with 5 cc. each of cooled acetic acid, alcohol, and ether. The precipitate is dried in a water oven to constant weight. Linseed oil yields from 23 to 38 per cent. of bromides; poppy, corn, cotton-seed, almond, olive, and in some cases tung oil, yield none; walnut oil 1.5–2.0, fish oil 49.0–52, Japan fish oil 22, cod-liver oil 30–43, shark-liver oil 19–22, seal oil 27, whale oil 15–25.

Boiled oils [2] can be detected by the lower percentage of bromides obtained in this test; where raw oil gives 24 per cent., boiled oils give from 8.4 to 21.

Chinese Wood Oil.—Percentage of oil in seeds 35 to 40.

Preparation.—This oil, called also Japanese Wood oil or Tung oil, is obtained from the seeds of the

---

[1] Analyst, 23, 313 (1898).

[2] Lewkowitsch, Analyst, 29, 334 (1904).

Elæococca vernicia, and must not be mistaken for gurjun balsam, also known as wood oil.

Properties.—It is pale yellow to dark brown, of unpleasant taste and odor. On exposure to light it is slowly changed to a solid fat, owing to the conversion of the elæomargarine into its isomer, elæostearine. It dries more rapidly than linseed oil, forming a hard film of little adhesive power to the surface beneath. It does not dry on the surface or in layers, as does linseed.

Composition.—It consists of the glycerides of oleic and elæomargaric acids.[1]

CHARACTERISTICS.

Sp. Gr. 15.5 °C.	Free Acid.	Iodine.	Saponification.
.939–.943	6.0	165[2]	190–195

When heated above 200° C. it gelatinizes and then neither melts nor dissolves.

Heating Test or Polymerization Test[3] (Browne).—This is used to show the presence of soy bean and other similar oils.

Test tubes for this test should be 16 cm. by 15 mm. with a mark near the bottom to indicate 5 cc. and closed by a cork with a 3.5 mm. hole in it, carrying a glass rod, 3 mm. in diameter. For a heating bath, a copper beaker 6 cm. in diameter and 12 cm. high, is filled with cottonseed oil to a depth of 7.5 cm.: this bath carries a thermometer 1.5 cm. from the bottom.

This thermometer may be a nitrogen filled ther-

---

[1] Cloez. Bull. Soc. Chem., **26,** 286 (1901); Compt. rend., 71, 649; **72,** 501.

[2] Hübl method, 18 hrs. A. S. T. M., 1918, 576.

[3] "Standards" A. S. T. M., 1916, 505; Chem. Abstr. **7,** 2315.

mometer 30 cm. long graduated from 100°–400° C. and should be corrected for stem exposure (p. 40). The oil bath is heated to 293°, and when very slowly rising at this point, the tube containing 5 cc. of the tung oil is placed in the bath so that the bottom is level with the end of the thermometer. Note the time, remove the lamp for about 45 seconds and replace it. Before two minutes have elapsed, the temperature of the bath will have fallen to 282°, at which point it should be kept as steady as possible. When the tung oil has been in the bath about 9 minutes, raise the glass rod at intervals of 30 seconds and when the rod is finally set, note the time. As setting or jellying takes place within a few seconds of fluidity, a good end determination is afforded. Remove the tube, heat the bath again to 293°, and repeat the test. The maximum length of time for raw tung oil is 12 minutes. No stirrer is used in the bath. A screen around the bath enables the temperature to be more easily reached. The oil bath requires renewing when tarry or viscid, otherwise the heating may be irregular.

Uses.—Wood oil cannot be regarded as a substitute for linseed oil; when mixed with it, it has given excellent results, especially for out-of-door work. When heated with driers at about 160° C. it has been used to good advantage in the manufacture of oil varnishes and enamel paints.[1] It is used as a floor varnish, in the manufacture of water-proof materials, and products resembling oilcloth.

---

[1] Toch, "Chemistry and Technology of Mixed Paints."

Soy Bean Oil.—Percentage of oil in seeds, 18 to 22.

Preparation.—This oil also called soja, soya, or Chinese bean oil, is obtained from the seeds of *soja hispida* or *japonica*, a plant native to China and Japan where the oil and press cake have long been used for food.

Properties.—It is pale yellow to brown.

Composition.—It consists of the glycerides of palmitic, oleic, linolic and linolenic acids.

CHARACTERISTICS.

Sp. Gr. 15° C.	Maumené.	Iodine.	Saponification.
.922–.927	87–88° C.	124–143	191–192

Uses.—It is used for soap making, and for boiled and blown oils, for grinding with colors, India rubber substitutes, etc. It occupies a position midway between cottonseed and linseed, either of which it can replace for soap manufacture. It dries slowly and is tacky. Satisfactory results can be obtained by boiling with a cobalt drier (Toch).

Poppy-seed Oil.—Per cent. oil in seeds 40–50.

Preparation.—Poppy-seed oil is prepared from the seeds of the common poppy.

Properties.—The "cold drawn" oil is colorless or pale golden yellow, that of the second pressing of a reddish color; the taste is pleasant, and it is practically odorless. It dissolves in twenty-five volumes of cold or six of boiling alcohol.

CHARACTERISTICS.

Sp. Gr. 15° C.	Maumené.	Iodine.	Saponification.
.924–.937	87° C.	133–143	190–197
.925		138	193

Adulterants.—The chief adulterant is *Sesame,* oil detected by the lower Iodine Value and Baudouin test.

Uses.—The oil is used as a salad oil and for mixing and grinding artists' colors.

Sunflower Oil.—Percentage of oil in seeds 30.

Preparation.—Sunflower oil is obtained from the seeds of the common sunflower.

Properties.—It is a pale yellow oil of bland taste and pleasant odor.

CHARACTERISTICS.

Sp· Gr. 15° C.	Maumené.	Iodine.	Saponification.
.924–.926	67°–75° C.	118–133	190–194

Gives Bechi but not Halphen or Baudouin test.

Uses.—For adulterating other oils, as olive, as an edible oil, for burning, soap- and varnish-making.

(2) Semi-drying Oils.

Corn Oil.—Percentage of oil in seeds 6 to 10.

Preparation.—Corn or Maize oil is prepared by expression from the germ of the corn separated in the manufacture of starch,[1] or from the residues from the fermentation of alcohol.[2]

Properties.—The former oil is pale to golden yellow, the latter reddish brown.

CHARACTERISTICS.

Sp. Gr. 15° C.	Maumené.	Elaidin.	Iodine.	Saponification.
.9215–.927	56°–88° C.	Pasty.	111–123	188–193
.922	85°		115	191
.922	100°		124	188[3]

---

[1] J. Soc. Chem. Ind., **11**, 286 (1892).

[2] Kriegner, Dingler pol. J. (1895), 39; abstr. J. Soc. Chem. Ind., **14**, 287 (1895).

[3] Boiled corn oil.

Adulterants.—Mineral and Rosin oils. These would be detected by the lowering of the characteristics (except Sp. Gr.), and the latter by the Liebermann-Storch reaction.

Composition.—It contains the glycerides of palmitic, arachidic, oleic, linoleic and, possibly, stearic acids.

Uses.—For adulterating other oils, as linseed, lard,[1] and olive, and for painting, burning, lubricating, and soap-making, especially soft and transparent soaps.

Cotton-seed Oil.—Percentage of oil in seeds 25.

Preparation.—Cotton-seed oil is obtained by pressing the seeds of the cotton-plant; when first pressed it is ruby-red or black, and is purified by treatment with caustic soda, carrying down the gelatinous substances and color as "cotton-seed foots." The grades in the market are Summer White and Summer Yellow, and Winter Yellow, according to the temperature or season of pressing.

Properties.—It is pale to deep yellow in color, and absorbs oxygen slowly from the air.

Composition.—It contains the glycerides of stearic, palmitic, oleic, linoleic acids, and some hydroxy-acids not yet investigated. (Hazura, Fahrion.)

CHARACTERISTICS.

Sp. Gr. 15° C.	Maumené.	Elaidin.	Iodine.	Saponification.
.9216–.930	70°–90° C.	Pasty.	101–117	191–196
.922	76°		108	

---

[1] Its presence can be told by the presence of sitosterol. See articles by Gill and Tufts, J. Am. Chem. Soc., **25**, 254 (1903). Also McPherson and Ruth, ibid., **29**, 921 (1907).

Adulterants.—It is rarely adulterated. Linseed oil is used for this purpose when the price permits.

Uses.—For adulterating other oils, as a cooking oil both by itself, also when hardened, and when mixed with suet, as "Cottolene," etc., and for soap stock; it, however, occasions a browning of the product.

Sesame Oil.—Percentage of oil in seeds 50–57.

Sesame oil, known also as Gingili or Teel oil, is prepared from the seeds of the sesame-plant.

Properties.—It is odorless, of a pale or deep yellow color and pleasant taste.

Composition.—It contains the glycerides of stearic, palmitic, oleic, and linolic acids, also other bodies[1] the composition of which is not exactly known, to which the color reaction (page 80) is probably due.

CHARACTERISTICS.

Sp. Gr. 15° C.	Maumené.	Elaidin.	Iodine.	Saponification.
.922–.924	65° C.	Pasty.	103–115	187–194

Adulterants.—Cotton-seed, Peanut, Rape, and Poppy-seed.

Cotton-seed oil would be shown by the special tests; *Peanut* oil by the low Specific Gravity and isolation of arachidic acid; *Rape* oil would lower all the characteristics and *Poppy-seed* oil raise them, especially the Iodine (138) and Maumené (87°) Values.

The Baudouin test (page 80) is the characteristic test for the presence of Sesame oil.

Uses.—It finds application as an edible and burning oil, also in tanning and soap-making.

---

[1] Bömer, Chem. Centralb., 70, ii. 729 (1899); Kreis, Chem. Ztg., 27, 1030, ibid., 28 956 (1904); Canzoneri and Perciabosco, Gaz. Chim. ital., 33, 253.

Rape-seed Oil.—Per cent. of oil in seeds 33–43.

Preparation.—This oil, otherwise known as Colza oil, is obtained from the seeds of *Brassica campestris* or its varieties, colza or turnip.

Properties.—It is of pale yellow color, peculiar odor, and harsh taste.

Composition.—The glycerides of stearic, oleic, erucic, rapic and arachidic[1] acids are contained in the oil.[2]

The free fatty acids vary from 0.5 to 6.2 per cent.

CHARACTERISTICS.

Sp. Gr. 15° C.	Maumené.	Elaidin..	Iodine.	Saponification.
.913–.917	49°–64° C.		94–106	168–178
.916	55°	Pasty.	101	174

Adulterants.—Cotton-seed, Poppy-seed, Hemp-seed, Linseed, and refined Fish oil.

Cotton-seed oil would be indicated by Maumené figure (76) and special tests; *Poppy-seed* oil by Iodine Value (138); *Hemp-seed* and *Linseed* by Specific Gravity (.934) and Iodine Value (176); *Fish* oil by the odor and high Iodine Value.

Rape-seed oil is distinguished by its almost complete insolubility in glacial acetic acid (Valenta test)[3] and by its high viscosity.

According to Palas,[4] if colza oil be agitated with rosaniline bisulphite, a rose-red coloration is obtained. Other oils of this and the preceding group

---

[1] Archbutt, J. Soc. Chem. Ind., **17**, 1009 (1898).

[2] Reimer and Will, Ber., **20**, 2388 (1887).

[3] American rape oils behave differently from the European, in being more soluble.

[4] Analyst, **22**, 45.

are unchanged, with the exception of linseed, which is changed to golden yellow. The reagent is prepared by mixing together in the cold, thirty cubic centimeters of a one per cent. solution of fuchsin, twenty cubic centimeters sodium bisulphite, 1.31 specific gravity, two hundred cubic centimeters water, and five cubic centimeters of sulphuric acid. The test is capable of detecting two per cent. of colza oil.

Uses.—It is used as a lubricant and a burning oil; because of the difficulty with which it is saponified it finds little application in soap-making.

Blown Rape-seed Oil.—See under Blown Oils, p. 135.

Castor Oil.—Percentage of oil in seeds 50.

Preparation.—Castor oil is obtained from the seeds of the castor-oil plant.

Properties.—It is colorless or pale greenish, of mild taste changing to harsh, especially with the American oils.

Composition.—It contains the glycerides of ricinoleic, dihydroxystearic, and stearic acids, and an active principle to which it probably owes its cathartic properties.

The free fatty acids vary from 0.7 to 14 per cent.; average about 1.

CHARACTERISTICS.

Sp. Gr. 15° C.	Maumené.	Acetyl Value	Iodine.	Saponification.
.959–.968	47° C.	150	81–90	176–186

Adulterants.—Blown oils, either Linseed, Rape, or Cotton-seed, and Rosin oils.

These, though but ten per cent. be present, cause a turbidity with absolute alcohol, with which castor oil is miscible in every proportion, as it is with glacial acetic acid. Rosin oil would be shown by the lowering of the saponification value.

Uses.—Castor oil is employed in the manufacture of Turkey red oil, for soap-making, illumination, and in medicine.

According to Lane[1] castor oil can be determined[2] in mixtures, soaps, and Turkey-red oils by making use of the fact that the lead soaps of this oil are wholly insoluble in petroleum ether of boiling point 28°–30° or 38°–40° C.

(3) Non-Drying Oils.

Almond Oil.—Percentage of oil in seeds 45 to 55.

Preparation.—Almond oil is obtained from the seeds of two varieties of the almond-tree, the sweet and bitter almond, the latter yielding the more oil.

Properties.—It is a bland thin oil of pale yellow color, mainly pure olein with some linolin.

CHARACTERISTICS.

Sp. Gr. 15° C.	Maumené.	Elaidin.	Iodine.	Saponification.
.914–.920 .918	53° C.	Solid.	93–102 97	190

Adulterants.—It is adulterated with Peach and Apricot Kernel oils, Cotton-seed, Peanut, Lard, Olive, Sesame, and Poppy-seed oils.

The first two are well-nigh impossible of detection. *Cotton-seed* oil would be indicated by the Maumené

---

[1] J. Soc. Chem. Ind., 26, 597 (1907).

[2] Also by the acetyl value.

figure (76) and Bechi or Halphen test. *Peanut* oil would be shown by the isolation of arachidic acid. *Lard* oil by the odor when heated and by the high melting point of the fatty acid (35° C.), and also *Olive* by the deposition of stearin when cooled to —5°. *Sesame* oil could be detected by the Baudouin test and *Poppy-seed* by the Iodine Value (138).

Uses.—Almond oil is used in medicine or whenever a fairly permanent oil is required.

Peanut Oil.—Percentage of oil in seeds 50.

Preparation.—By the cold pressing of the common peanut, a colorless, pleasant-tasting oil is obtained, which is used as a salad oil; a second pressing yields an oil of inferior quality, used as an edible and burning oil; a third pressing at a higher temperature yields a grade employed in soap-making.

Properties.—It varies in color from white to yellow.

Composition.—It contains the glycerides of palmitic, linolic, oleic, arachidic, and lignoceric acids.[1]

CHARACTERISTICS.

Sp. Gr. 15° C.	Maumené.	Elaidin.	Iodine.	Saponification.
.916–.921	45–75° C.	Solid.	85–105	189–197
.917	51°		98	194

Adulterants.—Cotton-seed, Rape, Sesame, and Poppy-seed are used to adulterate this oil.

Cotton-seed oil would be shown by the rise in the melting point of the fatty acids, those of peanut oil melting at about 28°, while those from cotton-seed melt about ten degrees higher; it would further be

---

[1] Gossmann and Scheven, Ann., **94**, 230 (1885); Kreiling, Ber. **21**, 880 (1888); Caldwell, Ann., **101**, 97 (1857).

shown by the special tests. *Rape* oil would be indicated by the low Saponification Value (175), *Sesame* oil by the Baudouin test, and *Poppy-seed* oil by the Specific Gravity (.924) and high Iodine Value (138).

Characteristic Test.—The oil can be detected in other oils by the isolation of its peculiar acid,—arachidic acid. This is effected, according to Renard's[1] process—as modified by Tolman[2]—as follows:

Weigh 20 grams of oil into an Erlenmeyer flask. Saponify with alcoholic potash, neutralize exactly with dilute acetic acid, using phenolphthalein as indicator, and wash into a 500 cc. flask containing a boiling mixture of 100 cc. of water and 120 cc. of a 20 per cent. lead acetate solution. Boil for a minute and then cool the precipitated soap by immersing the flask in water, occasionally giving it a whirling motion to cause the soap to stick to the sides of the flask. After the flask has cooled, the water and excess of lead can be poured off and the soap washed with cold water and with 90 per cent. (by volume) alcohol. Add 200 cc. of ether, cork, and allow to stand for some time until the soap is disintegrated; heat on the water-bath, using a reflux condenser, and boil for about five minutes.

disintegrated; heat on the water-bath, using a reflux condenser, and boil for about five minutes.

In the oils most of the soap will be dissolved, while in lards, which contain much stearin, part will be left undissolved. Cool the ether solution of soap to

---

[1] Renard, Compt. rend., 73, 1330 (1871); also Archbutt, J. Soc. Chem. Ind., 17, 1124.

[2] Bull. 107, U. S. Dept. Agriculture (1907), p. 145.

15° or 17° C. and let it stand until all the insoluble soaps have crystallized out (about twelve hours).

Filter and thoroughly wash the precipitate with ether. Wash the soaps on the filter back into the flask by means of a stream of hot water acidified with hydrochloric acid. Add an excess of dilute hydrochloric acid, partially fill the flask with hot water, and heat until fatty acids form a clear oily layer. Fill the flask with hot water, allow the fatty acids to harden and separate from the precipitated lead chlorid, wash, drain, repeat washing with hot water, and dissolve the fatty acids in 100 cc. of boiling 90 per cent. (by volume) alcohol. Cool to 15° C., shaking thoroughly to aid crystallization.

From 5 to 10 per cent. of peanut oil can be detected by this method, as it effects a complete separation of the soluble acids from the insoluble, which interfere with the crystallization of the arachidic acid. Filter, wash the precipitate twice with 10 cc. of 90 per cent. (by volume) alcohol, and then with alcohol 70 per cent. by volume. Dissolve off the filter with boiling absolute alcohol, evaporate to dryness in a weighed dish, dry and weigh. Add to this weight 0.0025 gram for each 10 cc. of 90 per cent. alcohol used in the crystallization and washing if done at 15° C.; if done at 20° add 0.0045 gram for each 10 cc. The melting point of arachidic acid thus obtained is between 71° and 72° C. Twenty times the weight of arachidic acid will give the approximate amount of peanut oil present. No examination for adulterants in olive oil is complete without making the test for peanut oil. Arachidic acid has a characteristic structure and can be detected by the microscope.

Uses.—These have been already given under the preparation.

Olive Oil.—Percentage of oil in the fruit 40 to 60.

Preparation.—Olive oil is prepared by expressing or extracting the fruit of the olive-tree; the oil varies greatly according to the tree, there being no less than three hundred varieties in Italy alone, and also the degree of ripeness and manner of gathering of the fruit itself.

Properties.—It varies in color from almost colorless to golden yellow or green.

Composition.—It contains palmitin, stearin, olein, and linolin,[1] the solid glycerides constituting about twenty-eight per cent. of the oil.

The free fatty acids vary from 1 to 24 per cent.

According to Allen, an oil containing more than five per cent. of free fatty acids is unfit for a lubricant, as it attacks the metals, and also, according to Archbutt, as a burning oil, as it causes charring of the wick.

CHARACTERISTICS.

Sp. Gr. 15° C.	Maumené.	Elaidin.	Iodine.	Saponification.
.914–.918	41°–47° C.	Very solid.	78.2–91.5	185–203
.916	35°		82	190

Adulterants.—Cotton-seed, Peanut, Rape, Sesame, Poppy-seed, and Lard.

Cotton-seed oil would be shown by the special tests and the high Maumené figure (76) and Iodine Value (108). *Peanut* oil by isolation of Arachidic Acid and

---

[1] Hazura and Grüssner.

high Iodine Value (98). *Rape* oil would be indicated by the Saponification Value (175) and Iodine Value (101). *Sesame* oil by the Baudouin test. *Poppy-seed* oil by the Iodine Value (138) and Maumené figure (87).

Olive oil is characterized by the low Maumené and Iodine Values and by the solid elaidin.

Uses.—It is used as an edible oil, for oiling textiles, as a soap stock, and as a burning oil.

ROSIN OILS AND TURPENTINE.

Rosin Oil.—Rosin oil is prepared by the distillation of common rosin (colophony) in stills holding about thirty barrels. About eighty-five per cent. of rosin oil and three per cent. of rosin spirits, or pinoline, are obtained. Acid water, gas, coke, and losses account for the remaining twelve per cent. The product obtained is a thick oil, known as "First Run;" this is redistilled, yielding a darker-colored oil, called "Second Run." This operation is repeated, yielding "Third," "Fourth," and even "Fifth Run."

The oil in the market is, however,[1] in nearly every case the product of a single distillation; upon distilling five to six thousand pounds of rosin the following yields are obtained.

Water	0.5 to 1 per cent.
Naphtha	1.5 to 2 per cent.
Raw oil	84 to 88 per cent.
Pitch	3 to 5 per cent.
Gases, loss, etc.	6 to 8 per cent.

---

[1] Spayd, Chem. Eng'r, 3, 218 (1905).

CHARACTERISTICS OF ROSIN OILS.

	Sp. Gr-15.	Maumené Figure	Iodine Number	Sapn. Number	Free Acid
1st Run	.975-.995		112-115		.05-4.8 per cent.
2nd "	.987	32°C	59	34	12.6
3rd "	.985	34°	77	25	13.7
4th "	.981	32.5°	23	20	9.6

When polarized in a 200 mm. tube it gives a reading from +30° to +40° on the Schmidt and Haensch sugar scale: other oils read between +1° and −1°.

Deodorized Rosin oil is that portion of the later runs which is freed from the "spirits" by fractional distillation.

Uses.—"First Run" is employed in making axle grease, in oiling leather, and making cements. "Second Run" finds use in printing ink and in the leather industry. "Third" and "Fourth" runs are used mainly for mixing with other oils.

Qualitative Test.—Rosin oil may be detected by the Liebermann-Storch reaction.[1] One to two cubic centimeters of the oil are shaken with an equal quantity of acetic anhydride and gently warmed. When cool, the acetic anhydride is pipetted off and tested by the addition of one drop of concentrated sulphuric acid. A fine violet color is produced in the presence of rosin oil.[2] Cholesterol which is contained in the

---

[1] Storch, J. Soc. Chem. Ind., 7, 136 (1888).

[2] And sometimes by Chinese wood oil.

animal fats produces a similar coloration; this can be removed by saponifying the oil as completely as possible and shaking out the somewhat dilute soap solution with ether or petroleum ether. The soap solution is then acidified, setting free the fatty acids, and these treated with acetic anhydride as if they were the oil.

Renard's test modified by Allen[1] consists in adding a few drops of stannic bromide, dissolved in carbon bisulphide, to a few drops of the oil, also dissolved in carbon bisulphide. Should rosin oil be present a violet color will be produced, which on standing forms a deposit at the bottom of the tube. Glacial acetic acid is recommended as a solvent in the case of mineral oils, these not dissolving it to any appreciable extent and not masking the reaction.

Wiederhold[2] states that rosin oils are dissolved at 15° C. by half their volume of anhydrous acetone, while mineral oils, especially American, are almost unacted upon by it.

Rosin Spirits.—Its preparation has already been given under rosin oils.

Properties and Composition.—It has a peculiar odor and contains heptine,[3] C_7H_{12}, which boils at 103–104° C. and absorbs oxygen readily.

CHARACTERISTICS.

Sp. Gr. 15° C.	Maumené.	Iodine.
.856–.883	91° C.	185

---

[1] Commercial Organic Analysis, ii. 463.

[2] Z. anal. Chem., 33, 111 (1894).

[3] Veitch, Bureau of Chemistry Circular No. 36, p. 31 (1907).

The boiling point varies from 80° to 250° C. The free acid is sometimes 15 per cent.

Valenta[1] states that rosin spirits, or "essence of turpentine" as he calls it, can be distinguished by the following reactions: (1) acetic anhydride and one drop of sulphuric acid give an intense green color; (2) one part of oil and 1 to 2 parts of a 6 per cent. solution of iodine in chloroform or carbon tetrachloride, warmed gently on a water-bath, give intense green to olive-green colors. The strongest colors are given by the lower boiling fractions. This last reaction is not given by oil of turpentine (gum), pine resin oils (wood turpentine), light petroleum, oil of camphor, or rosin oil.

Adulterants.—Petroleum and shale products.

Uses.—As a substitute for gum turpentine.

Turpentine.—*Preparation.*—Turpentine is prepared[2] by distilling pine resin in copper stills of about eight hundred gallons' capacity; the process requires some care to prevent overheating and obtain a fine quality of rosin. To aid the process, after the crude resin is melted, a stream of tepid water from the condenser is run into the still, thus making a distillation with steam. The yield and quality vary according to the length of time the trees have been producing resin, both growing inferior with age. The crude resin, or "dippings," of the first season is

---

[1] Chem. Zeit., 29, 807 (1905); abstr. Analyst, 30, 342.

[2] Condensed from a monograph on "The Timber Pines of the Southern United States," by Filibert Roth, U. S. Dept. of Agriculture (1896). Also "Commercial Turpentines" Veitch & Donk U. S. Dept. Ag., Bureau Chem. No. 135 (1911). See also Schorger, J. Ind. Eng. Chem. 6, 541 (1914).

called "virgin dip," and produces the finest quality of rosin, W. W. (water white) and W. G. (window glass); the better grades are N, M, and K, passing through the poorer grades to the black A. From two hundred and twenty-five barrels of soft turpentine and one hundred and twenty barrels of hard gum, the product of a second season, nineteen hundred gallons of turpentine and two hundred barrels of amber rosin, I, H, or G, were produced.

The resin is chiefly obtained from the Long-leaf Pine, *Pinus palustris* or *australis*, known also as Southern, Yellow, or Hard Pine.

Properties and Composition.—Turpentine is a colorless liquid of peculiar taste and odor. On exposure to the air, it absorbs oxygen and gradually becomes resinous. It consists mainly of a hydrocarbon, Pinene, $C_{10}H_{16}$.

The specifications of the American Society for Testing Materials[1] apply to either gum or wood turpentine, and are as follows: "It shall be clear and free from suspended matter and water. The color shall be "standard," (that is, in a depth of 50 mm. approximately match a No. 1, Yellow Lovibond Glass) or better. The specific gravity shall not be less than 0.862 nor more than 0.872 at 15.5° C. The refractive index at 15.5° C. shall not be less than 1.468 nor more than 1.478. The initial boiling point shall not be less than 150° nor more than 160° and 90 per cent., shall distil below 170°. The polymerization residues shall not exceed 2 per cent. and its

---

[1] A. S. T. M. "Standards" (1918), 581 (1920), 680.

refractive index shall not be less than 1.5." The iodine member varies from 331[1] to 391[2]. The flash point is 83° to 95° F. by the New York State Board of Health tester. American turpentine deflects polarized light to the right, although a sample obtained from spruce-trees had a specific rotation of —40.79.[3]

Adulterants.—Petroleum and Shale Products, Rosin Spirits, Wood[4], and Russian Turpentine are the chief adulterations.

Petroleum and Shale Products: The lighter ones would be indicated by the lowering of the specific gravity, flash test, and iodine value, they having a value of 30 and 70 respectively, and by distillation. Kerosene might be detected by the "bloom." To determine the quantity of petroleum or heavy oil added, the sample should be treated with sulphuric acid.

Polymerization Test.[5]—Measure 20 cc. 38N (100.92 per cent.) sulphuric acid into a graduated Babcock flask, stopper, and cool in ice water. Add slowly 5 cc. of the turpentine and gradually mix the two, cooling from time to time, not allowing the temperature to rise above 60°. When the mixture no longer warms up on shaking, shake thoroughly and heat it in a water bath to 60°–65° for about 10 minutes, keeping the mixture thoroughly mixed by thorough shaking, five or six times. Do not stopper the flask after addition of the turpentine, as it may explode.

---

[1] Wilson, Chem. Trade J., **6**, 316; J. Soc. Chem. Ind., **9**, 657 (1890).

[2] Worstall, ibid., **23**, 302 (1904).

[3] Long, J. Am. Chem. Soc., **16**, 844 (1894).

[4] McCandless, ibid., **26**, 981 (1904).

[5] A. S. T. M. op. cit 583.

Cool to room temperature, fill the flask with the sulphuric acid until the oil rises into the graduated neck and centrifuge at 1200 r.p.m. for 5 minutes, or allow to stand 12 hours. Read the volume of the residue, note its consistency and color, and determine its refractive index.

Distillation Test.[1]—100 cc. of turpentine are distilled as in the case of kerosene (p. 18) using however an oil bath. The Engler flask is fitted with a thermometer reading from 145°–200°, so that the bulk shall be opposite the side tube of the flask and the 175° mark below the stopper. Conduct the distillation so that the distillate passes over at the rate of 2 drops per second. Note the initial distilling temperature and the per cent. distilling below 170.°

Rosin Spirits could be detected by distillation and treatment of the residue with stannic bromide (Renard's test, p. 128) dissolved in carbon bisulphide and also Valenta's test, p. 54. The addition of rosin spirits or wood turpentine is readily shown by Herzfeld's test, the production of a yellow color by shaking with a solution of sulphurous acid. They would also cause a lowering of the iodine value, that for rosin spirits being 185[2] and refined wood turpentine 212.[3]

McCandless[4] claims to detect the latter by distilling the turpentine according to Engler's method for kerosene, p. 18, and determining the refraction index of various distillates. "The flame used must

---

[1] A. S. T. M. op. cit. 582, also Bull. 898 U. S. Dept. Ag., 1920.

[2] Am. Chem. J., 12, 102.

[3] Loc. cit.

[4] Worstall, loc. cit.

be small, the thermometer rise very slowly, and the first half cubic centimeter of the distillate collected by itself, the refractive index being taken at 25° C. In case of no genuine oil will this fall below 1.4659, being usually 1.4665 to 1.4678. Several samples of wood turpentine show readings as low as 1.4652, 1.4646, or even 1.4639. When the wood turpentines do not show a low initial reading, they nearly always show a high reading on the final portion of the distillate. I have adopted the 97th and 98th cc. as being in practice the most convenient to collect separately for the purpose of making the final refractive index. In the case of the genuine (gum) spirits this reading will not exceed 1.4765, usually much less, but with wood turpentine will exceed 1.4765 and may even reach 1.4840. A further distinction between genuine and wood turpentine may be observed during this distillation; in nearly all genuine spirits 95 per cent. will have distilled over by the time the temperature reaches 165° C., whereas with wood turpentine, when 95 per cent. have come over, the thermometer is much higher than 165°."

Paul[1] says the above method is fairly satisfactory.

Besides this method Geer[2] recommends the fractional distillation with steam.

Russian Turpentine would be shown by the higher temperature of distillation, 170° to 180°. Pure tur-

---

[1] J. Ind. and Eng. Chem. 1, 27 (1909).

[2] U. S. Dept. Agriculture Forest Service Circular 153 (1908).

pentine should leave no residue upon writing-paper after half an hour.

Uses.—Turpentine finds extended use as a solvent for fats, waxes, resins, and rubber, and as a "drier" in paints.

Wood Turpentine.—Wood Spirits, Stump Turpentine.—As its name denotes, this is obtained by distilling pine wood ("light wood," stumps, knots, etc.) with steam: superheated steam was formerly employed, but modern practice uses direct steam, postponing destructive distillation or any other process until the spirits are first removed. The wood is chipped as for the manufacture of wood pulp, filled into horizontal or vertical retorts, and steam blown into them: this requires from one to twelve hours and the yield is from 6 to 25 gallons per cord, the average being 12 to 15 gallons. When the stills are properly operated and the product is suitably refined, there should be practically no difference between the turpentine prepared in this way and the ordinary (gum) turpentine.[1]

Properties.—It has a specific gravity of 0.862 to .870 at 15.5° C., and 90 per cent. should distil between 150° and 170° C.[2] and an iodine number of 212 to 352.[3]

Adulterants and Uses.—The same as for gum turpentine, which see. On account of the odor of

---

[1] Teeple, J. Soc. Chem. Ind., 26, 811 (1907), also Adams J. Ind. & Eng. Chem. 7, 957.

[2] "Wood Turpentine," Veitch & Donk, U. S. Dept. Ag. Bureau Chem. Bull. 144 (1911).

[3] McCandless, loc. cit.

some varieties it is better used for out-door painting than for inside work.

Varieties of Turpentine and Sources.—American turpentine, from *Pinus palustris* or *australis*, the Longleaf Pine, dextrorotary.

English turpentine, from gum collected in America, from *P. australis* and *P. tæda*, Loblolly.

French, from *Pinus maritima*, Sea-pine, and *P. glabra*, Spruce Pine, lævorotary.

German, from *P. sylvestris*, Scotch Pine or Fir, *P. nigra*, Black Pine, and *P. rotundata.*

Venice, from *Larix europœa*, Larch.

Russian, from *P. sylvestris*, and *P. ledebourii*, dextrorotary.

Blown Oils.—*Preparation.*—Blown, Base, Thickened, or Oxidized oil is usually prepared by heating the oil to 70° or 110° in a jacketed kettle and forcing a current of air through it; after the action is once started no further heating is usually necessary.

Properties.—The color of the oil darkens slightly and the density and viscosity are much increased. Benedikt and Ulzer think that the fatty acids are oxidized to hydroxyacids. The oils submitted to this process are chiefly Rape and Cotton-seed, although it is often applied to Linseed, Sperm, and Seal oils.

CHARACTERISTICS.

Sp. Gr. 15° C.	Maumené.[2]	Iodine.	Saponification.
.967	253–(57°)	63.6	197.7 Rape.
.974	227	56.4	213.3 Cotton-seed.
.980	...	90.7	208.6 Maize.

---

[1] Thomson and Ballantyne, J. Soc. Chem. Ind., **11**, 506 (1892).

[2] Specific temperature reaction.

Uses.—On account of their high viscosity, blown oils are used to mix with other oils for lubricating purposes.

Palm Oil.—*Preparation.*—Palm oil is obtained from the flesh or pericarp of the palm-nut; this grows in immense quantities on the west coast of Africa. The fruits are fermented, whereby the oil rises to the top, or it is expressed from the fresh fruit. The latter process yields the finer and more fluid product.

Properties.—Owing to its method of preparation its properties are quite varied. It is of a buttery or tallowy consistency, of orange-yellow to dirty red in color, and has an odor in some samples recalling that of violets. By heating to a high temperature or treatment with acids it may be bleached.

Composition.—It is mainly palmitin, with some olein and free palmitic acid.

CHARACTERISTICS.

Sp. Gr. 99° C.	Iodine.	Saponification.
.859	53–56	196–202

Adulterants.—Water and dirt, mostly sand.

Characteristic Test.—It was thought until recently that there was a characteristic test for palm oil.[1] It resembled the Lieberman Storch test (p. 127), giving a blue instead of a violet color. Gill[2], however, showed that the test was really one for carotin, which palm oil was found to contain in considerable

---

[1] Crampton and Simons, J. Am. Chem. Soc., 27, 272 (1905).

[2] J. Ind. & Eng. Ch. 9, 136 (1917); *id.* 10, 612 (1918).

quantity. He has also found it present in linseed, mustard, sesamé and corn oils.

Palmer and Eckles[1] showed carotin also present in animal fats and oils, as oleo oil and butter. Consequently the test cannot be used to show the presence of palm oil where any of these oils is known to be present.

Uses.—For the manufacture of soap and candles and coloring other oils.

Cocoanut Oil.—*Preparation.*—Cokernut oil is obtained from the fat of the cocoanut, the fruit of species of palm. The finest quality is that prepared in Cochin (Malabar) from the fresh fruit. Inferior varieties are made from the dried kernels, or "coprah," which contain 60 to 70 per cent. of oil.

Properties.—It is a solid white fat of bland taste and peculiar odor, readily turning rancid. It is soluble in two volumes of absolute alcohol at 31° C.

Composition.—It contains a larger proportion of insoluble volatile acids than most oils; the glycerides of caproic, caprylic, capric, oleic, lauric, and myristic acids are among those present.

CHARACTERISTICS.

Sp. Gr. 99° C.	Iodine.	Saponification.
.874	8–10	253–268

Adulterants.—It is rarely adulterated.

Characteristeric Test.—Hanus[2] has devised a method for the detection of this fat in other fats and oils

---

[1] J. Biol. Chem., **17**, 190–249 (1914).

[2] Hanus, Z. Nahr, und Genussm., **13**, 18 (1907), **16**, 577 (1908).

based upon the volatility of the ethyl esters made from the acid in cokernut oil, the "ethyl ester number." The procedure is as follows: five grams of the melted fat are weighed into a 200 cc. Erlenmeyer flask, and heated for fifteen minutes in an oven at 50° C.; exactly 30 cc. of $\frac{N}{10}$ alcoholic potassium hydroxide solution are then added from a burette, and the mixture is thoroughly shaken until perfectly clear, usually about two minutes. After keeping the contents of the flask at a temperature of 50° C. for eight minutes, 2 cc. of dilute sulphuric acid are added, the acid being of such concentration that the 2 cc. will exactly neutralize the 30 cc. of potassium hydroxide solution. The contents of the flask are now diluted to a volume of 145 cc. with water, a few pieces of quenched pumice are added, and the mixture is distilled, using a fusible metal bath and single bulb tower. The first 30 cc. of alcoholic distillate which comes over is collected in a graduated cylinder, the next 100 cc. of distillate being received separately in a 100 cc. flask. The whole distillation must not take longer than twenty-five minutes. Both fractions of the distillate are now transferred to two separate flasks; alcohol is added to the aqueous distillate until a clear solution is obtained, the free acidity of both portions is neutralized, using phenolphthalein as an indicator, and they are then boiled with 40 cc. of $\frac{N}{2}$ alcoholic potassium hydroxide solution. After titrating back the excess of alkali, the number of cc. of $\frac{N}{10}$ alkali required for the saponification of the esters from 5 grams of the fat is calculated from the $\frac{N}{2}$ used.

For cokernut oil the number of cubic centimeters of $\frac{N}{10}$ alkali required for the saponification of the esters in the alcoholic portion is from 38 to 44, butter 8–9.4, lard 1.6. Palm oil, 23.1. Cocoa butter 1.3–1.6.

It can also be detected by the Polenske number, which is the number of cubic centimeters of alkali required to neutralize the insoluble volatile fatty acids distilled from 5 grams of fat. It is determined like the Reichert-Meissl number, p. 172. The description would take us beyond the limits of this volume and reference may be had to Woodman's "Food Analysis," p. 207.

Uses.—It is used in soap-making (marine soaps), in candle-making, and as an edible fat.

CHAPTER VII.

ANIMAL OILS.

(1) Marine Animal Oils.

a. Fish Oils.

Menhaden Oil.—This oil is otherwise known as mossbunker, pogy, porgy, or whitefish oil.

Preparation.— It is prepared from the menhaden by steaming and expression. There are several grades in the market, differing in appearance according to the source from which they are derived. They are Select Light Strained, Select Light, Choice Brown, Dark, and Gurry oil. The better varieties are obtained by gentle pressure and subsequent bleaching, and the others by the pressing of the residues.

Properties.—It is yellow to brown in color, and oxidizes readily on exposure to the air.

It is to be noted, however, that the firm, hard coating or "skin" which is formed on drying is usually not as closely adherent to the surface beneath it as that formed with linseed oil.

Composition.—It apparently contains the glycerides of myristic, palmitic, stearic, and unsaturated acids of C_{18}, C_{20} and C_{22} atoms[1], and also isocholesterol.

CHARACTERISTICS.

Sp. Gr. 15° C.	Maumené.	Elaidin.	Iodine.	Saponification.
.927–.933	123°–128° C.	Liquid.	139–172	189–192
.930	126		154	190

---

[1] Twitchell J. Ind. & Eng. Ch. 9, 581 (1917).

Adulterants.—The chief adulterant is Mineral oil, which would be shown by a lowering of all these characteristics.

Uses.—It is used[1] in currying, for adulterating other oils, as linseed, whale, and sardine, as a substitute for linseed oil, and as a burning oil for mines.

REFERENCE.

G. B. Goode, "The Natural and Economic History of the American Menhaden," U. S. Commission of Fish and Fisheries, vol. v., 1879.

β. Liver Oils.

Cod Oil.—Three varieties of cod or cod-liver oil are obtainable in the market, the *pale yellow,* or "steam rendered," and the *light brown,* both of which are used in pharmacy, and for the examination of which recourse must be had to larger works. The other, the *brown* oil or "cod oil," used in currying, may be derived from the liver of any fish, hence it is impossible to give any data upon which judgment may be formed.

γ. Blubber Oils.

Whale Oil.—*Preparation.*—Whale or Train oil is obtained by rendering the blubber of various species of whales except the sperm and bottlenose.

Properties and Composition.—It has a strong fishy odor, a "nutty" taste, and is of a light-yellow to yellowish-brown color. Little is known regarding its constitution. As may be expected, its composition varies widely.

---

[1] For its detection see Eisenschiml and Copthorne, J. Ind. and Eng. Chem., 2, 43 (1910).

CHARACTERISTICS.

Sp. Gr. 15° C.	Maumené.	Iodine.	Saponification.
.917–.930	85°–91° C.	110–136	188–193
.927	88°	120	190

Adulterant.—It is largely adulterated with Seal oil, which there is little chance of detecting.

Uses.—Whale oil is used as a leather dressing, as a burning oil, and to mix with other oils as a lubricant.

(2) Terrestrial Animal Oils.

Neat's-foot Oil.—*Preparation.*—Neat's-foot oil is obtained from the feet of neat cattle. The hoofs are separated, the bones of the foot disjointed, and the latter boiled with water, the emulsion allowed to settle, and the oil which rises separated. As is the case with all oils, that which is obtained by the least degree of heat or pressure is the best.

Properties.—It is of a light-yellow color, bland taste, possesses a peculiar odor, and little tendency to turn rancid.

Composition.—It is nearly pure olein, containing a small quantity of stearin, which it frequently deposits. The free fatty acids may amount to six per cent.

CHARACTERISTICS.

Sp. Gr. 15° C.	Maumené.	Elaidin.	Iodine.	Saponification.
.914–.916	42–49.5° C.	Solid at times.	66–76	194–199

If the iodine number be less than 63, it probably contains hide oil. The fatty acid should be less than one per cent. Titer test may be from 17° to 26°.

Adulterants. — Fish, Poppy-seed, Rape, Cotton-seed, Mineral oils, and other hoof oils.

Fish oil would be shown by the Iodine Value and Maumené test, also by the odor when heated; *Poppy-seed* oil by the Gravity (.925) and Iodine Value (138); *Rape* oil by Saponification (175) and Iodine Value (101); *Cotton-seed* by the special tests and Iodine Value (108); *Mineral* oil by the lowering of all the characteristics given.

Uses.—Neat's-foot oil finds application as a lubricant, either by itself or mixed with other oils, and for currying purposes.

CHARACTERISTICS.

Sp. Gr. 15° C.	Maumené.	Iodine.	Saponification
.916–.922	46°–55° C.	75–86	197.1

It is used for mixing with and adulterating other oils, as, for example, neat's-foot; when refined it has been used to adulterate olive oil.

Lard Oil.—*Preparation.*—Lard oil is obtained by pressing lard; upright screw-presses are used and a pressure of about eight thousand pounds to the square inch employed; from forty to sixty per cent. of the lard is obtained as oil.

Brands.—These vary according to the source whence they are derived; the various lards in the American market are: *Neutral Lard,* obtained from the "leaf" by rendering at a low temperature (105° to 120° F.), used in making butterine. Only a portion of the fat is thus extracted; the operation is then completed, yielding *Leaf Lard. Choice Lard* is obtained from some parts of the leaf and fat from the backs. *Prime Steam Lard* is the product obtained from the trimmings, head, heart, and some intestinal fat. *Gut Grease* is obtained by rendering all the other parts of the hog except the heart, liver, and lungs.[1]

Besides these products obtained from the live hog, there are *Butchers' Lard* or *Crackling Grease,* obtained from scraps and trimmings, and *White Grease* and *Brown Grease,* which are obtained from hogs dying in transit, being prepared from the eviscerated animal and its viscera respectively. Lastly, there is *Yellow Grease,* a product of the refuse of the packing-houses.

All but the first two lards are pressed, yielding an oil which is classed according to its color as "Prime" (very light straw) to "No. 2" (brown).

The varieties in the market are as follows: "Prime" Lard oil, prepared from Prime Steam Lard; "Pure" Lard oil, from No. 1 Lard and White Grease; "Extra No. 1," from Light Yellow Grease; "No. 1," from Yellow Grease; "No. 2," from Brown and Gut Grease; and "Crackling Oil," from Crackling Grease.

Properties.—The color varies from very light straw to brown, and the odor from almost none to offensive in the No. 2 lards.

Composition.—Its chemical composition is largely olein, with admixture of stearin and palmitin.

---

[1] Condensed from "Lard and Lard Adulterations," by H. W. Wiley, U. S. Dep't Agriculture, Bull. 13, 1889, p. 14.

CHARACTERISTICS.

Sp. Gr. 15° C.	Maumené.	Elaidin.	Iodine.	Saponification.
.914–.916	39° C.	Solid cake.	60	195–6.[1]
	41		72.5[2]	
	43		75[3]	

Various parts of the animal give oils which vary considerably; the iodine values of oils from different sources are as follows[4]:

Leaf.	Intestine.	Back.	Foot.	Head.
52.5–53	57.3	60.6	77.3	85

Adulterants.—These are Cotton-seed, Corn, and Neutral Petroleum oils.

Cotton-seed oil would be shown by the Elaidin, Maumené, and special tests. *Corn* oil would be indicated by the Maumené test (58) and Iodine number (115). *Petroleum* by the flash test and lowering of the characteristics.

Uses.—Lard oil is used as a burning and lubricating oil, as an edible oil, and for oiling textile material preparatory to spinning.

REFERENCE.

Wesson, Jour. Am. Chem. Soc., **17**, 723–735 (1895).

Tallow Oil.—*Preparation.*—Tallow oil is prepared by pressing tallow after the manner of lard, which see.

Properties.—It is a light-yellow bland oil, and of an odor resembling tallow.

CHARACTERISTICS.

Sp. Gr. 15° C.	Maumené.	Elaidin.	Iodine.	Saponification.
.916	35	Solid cake.	56	197

---

[1] No. 2 lard. [2] No. 1 lard. [3] Prime lard. [4] Wiley, *loc. cit.*

Uses.—It is used to mix with other oils and as a lubricant.

Elain or Red Oil.—*Preparation.*—Elain oil, or, as it is sometimes called, "Saponified Red oil," is obtained by the saponification of the solid fats by the lime, sulphuric acid, or water methods. The fatty acids thus freed from their combination with glycerin are allowed to solidify and are pressed. According to the temperature, more or less stearic and palmitic acids go into the product; these can be separated by distillation.

It is oftentimes semi-solid, resembling tallow; the distilled varieties are light brown to deep red.

Composition.—Chemically speaking, it is nearly pure oleic acid.

CHARACTERISTICS.

Sp. Gr. 15° C.[1]	Free Fatty Acids.	Iodine.	Saponification.
.899–.908	80–97	90[2]	200

It may contain some unsaponifiable matter, consisting of hydrocarbons formed in the process of distillation; these may vary from three to seven per cent.

Uses.—It is used for oiling wool, as it readily saponifies, and in soap-making.

---

[1] Allen, Lewkowitsch.

[2] Iodine number of the pure acid.

B. WAXES.

LIQUID WAXES.

Sperm Oil.—*Preparation.*—The real sperm oil is obtained from the great cavity in the head of the sperm whale; it is often mixed with the oil obtained from the body, or "blubber oil." The process of manufacture consists in chilling the crude oil, separating the spermaceti by pressure, and bleaching the expressed oil in thin layers by exposure to the sun.

Properties.—It is a limpid, pale-yellow oil of faint odor and taste.

Composition.—It contains no glycerides (Allen, Lewkowitsch), but is a mono-ester, a compound of an alcohol[1] and an organic acid.[1] When saponified these alcohols are freed, and the oil yields forty per cent. of unsaponifiable matter. It may contain two per cent. of free fatty acids.

CHARACTERISTICS.

Sp. Gr. 15° C.	Maumené.	Elaidin.	Iodine.	Saponification.
.844–.884	45°–47° C.	Solid at times.	81–90	123–147
.880			(70)	

Adulterants.—Owing to its high cost it is often adulterated, Whale, Mineral, Rape, Liver, and

---

[1] Cetyl alcohol, $C_{16}H_{33}OH$, and palmitic acid have been identified in the oil.

Arctic Sperm (bottlenose whale) oil being used for this purpose.

Whale oil would be shown by the strong fishy odor and "nutty" taste, also by the raising of all the constants. *Mineral* oils would be indicated by the low flash point, corresponding to a gravity of 0.880, and by the lowering of the characteristics. *Rape* oil by the high Saponification Value (175) and the isolation of the glycerin, which when multiplied by ten gives the fatty oils. *Liver* oils would be revealed by the violet coloration with sulphuric acid and rise in the constants. *Arctic Sperm* oil might be shown by the taste.

Uses.—It is employed as a lubricant; the viscosity is less than any other non-drying fatty oil, and also varies less than any other oil with increase of temperature.

REFERENCES.

Starbuck, "History of American Whale Fishery from Earliest Inception to 1875."

Report of U. S. Commissioner of Fisheries, vol. iv., 1875.

Scammon, "Mammalia of North-Western America."

CHAPTER VIII.

RECOVERED AND WASTE OILS AND FATS. LUBRICATING GREASES. MISCELLANEOUS OILS.

Edible Fats. Hardened Oils.

THESE have assumed more importance of late in this country, particularly with the increasing requirements of boards of health that these substances be kept out of the brooks and rivers. Some of them are:

- Wool Fat,
- Distilled Grease Oleines,
- Sod Oil,
- Cotton-seed Foots,
- Fuller's Grease,
- Black Oil,
- Garbage Grease.

Wool Fat.—British, German, or American Degras, Suint; Lanoline; Wool, Recovered, or Yorkshire Grease.

Preparation.—As the names denote, this is the greasy material obtained in the washing of wool:[1] wool contains from 30 to 80 per cent. of impurities, made up of (a) wool grease, the fatty matter secreted by the skin of the sheep, amounting to 6 to 17 per cent. of the wool; (b) suint, also a skin secretion but soluble in water, consisting of the potassium salts of oleic, valeric, and acetic acids, with sulphates, phosphates, chlorides, and nitrogenous compounds amounting to 5 to 24 per cent. of the wool;

---

[1] For a detailed description of wool-washing, see Thorp's "Outlines of Industrial Chemistry."

and (c) dirt, earthy matter, and manure. These are removed in two ways, by scouring with soap and alkali, and by extraction of the grease with solvents, usually naphtha or carbon tetrachloride, and subsequent washing. These foul and ill-smelling wash-waters are usually run into the streams and form one of the most troublesome sources of pollution. Wool grease is difficultly saponifiable but readily emulsifiable and is deposited the entire length of the stream.

To recover the grease, the wash-waters are allowed to stand, to settle out the sand and dirt, then "soured" with sulphuric acid, whereupon part of the grease floats and part settles; these portions are collected and pressed hot through canvas. The grease thus obtained contains besides wool grease, the fatty acids of the soaps used and also traces of sulphuric acid. Or the solvent is distilled off from the solution of the grease and the latter strained into barrels. The product thus obtained is of lighter color and better quality than that obtained in the acid process, is free from sulphuric acid and practically so from fatty acids, and is the only one to which the term wool grease is properly applied.

Properties.—It is a light or dark brown substance of peculiar, unpleasant odor and salvy consistence; it is not wholly saponified by alcoholic potash, requiring sodium alcoholate to complete the process. It mixes with water readily and forms emulsions which are unusually permanent, particularly if any alkali be present, and which may contain as much as 80 per cent. of water. It is not readily oxidized on exposure to the air.

Composition.—It is a complex mixture of alcohols and esters, a collection of waxes and not a fat: the esters are largely those of cholesterol and its isomers. Lanoceric, lanopalmic, myristic, carnaubic, and other oily and volatile acids, ceryl and carnaubyl, alcohol, cholesterol, and isocholesterol are some of the compounds which have been found in the grease.

CHARACTERISTICS OR CONSTANTS.

From what has been said, it will be seen that it is impossible to give any figures to which the name constant can properly be applied.

Sp. Gr.	Iodine.	Saponification.
$\frac{100°C.}{15.5°}$ 0.9017	26	98–102

ANALYSIS OF WOOL GREASE IN PER CENT.

Water.	Fatty acids.	Neutral oil.	Unsaponifiable.
1	19–26	68–17	12–56

Adulterants.—It is rarely adulterated, the usual one being mineral oil, not intentionally added but coming from the wash-waters. It could be detected by its resistance to saponification and insolubility in acetic anhydride, which converts the cholesterol into the acetate. Rosin oil might also be used and could be detected by partial saponification with potash, the object being to saponify the rosin acids in the oil and not the cholesterol esters, and the liberation of the rosin acids, which are submitted to the Liebermann-Storch test.

Uses.—Degras is used to mix with oils for currying purposes, with lard and similar oils for "wool oils," and when purified forms the Lanoline of the Pharmacopœia. This, from the ease with which it is absorbed by the skin, makes an admirable basis for salves and ointments. There are two varieties, one anhydrous (adeps lanæ), and one with about 25 per cent. of water or Lanoline proper. It is used to replace tallow in certain cylinder oils.

Distilled Grease.—*Preparation.*—This is prepared by distilling wool grease in cast-iron stills, using superheated steam to carry forward the heavy vapors. A "stearine" and "oleine" are obtained by cooling and pressing the distillate. Wool fat pitch is left in the retort.

Properties.—The crude stearines are brownish and, like all these products, of a peculiar penetrating aldehydic odor; they are refined and are then white and crystalline. The oleines are light yellow to dark brown and have a greenish fluorescence, which must not be mistaken for the bluish "bloom" of the mineral oils used as adulterants.

Composition.—The esters originally present in the wool fat are broken down into hydrocarbons and fatty acids of high molecular weight, stearic, palmitic, and oleic, which in turn are dissociated into acids of lower molecular weight and other hydrocarbons. The following equation, cited by Smith,[1] gives an idea of what may have taken place:

---

[1] Ann. Chim. Phys. (3), 6, 40.

$$C_{15}H_{31}COOC_{16}H_{33} = C_{15}H_{31}COOH + C_{16}H_{32}$$
Cetyl palmitate = Palmitic acid + Cetene

These hydrocarbons have been investigated by Gill and Forrest.[1] They were found to be olefines, from hepta decylene, $C_{17}H_{34}$, Bpt. at 1 mm. 95°–100°, an oil, to triacontylene $C_{30}H_{60}$, Bpt. 186°–193°, a wax-like solid. They can be distinguished from hydrocarbons intentionally added, by the determination of the bromine addition and substitution numbers, the optical rotation, and index of refraction. These constants, obtained on hydrocarbons separated from some distilled grease oleines by Gill and Mason,[2] are shown in the table below.

Oleine.	Sp. Gr.	Bromine. Addition.	Bromine. Substitution.	Optical Rotation.	Refractive Index at 20° C.
A	0.896	28.8	14.2	+17° 58′	1.4967
B Pure	0.902	25.1	14.8	17° 36′	1.4991
C	0.896	21.5	16.8	15° 13′	1.4948
Mineral oils	0.848 to 0.863	4.4 to 5.9	5.6 to 8.4	1° 25′	1.4662 to 1.4750

The extraction of the unsaponifiable matter is carried out as follows: 200 grams of the oil are saponified by boiling on a water-bath two or three hours with an excess of alcoholic potash (120 grams to the liter) in a 750 cc. flask, provided with a return flow condenser. When the saponification is complete the solution is transferred to a liter separatory funnel and shaken several times with 300 to 400 cc. of redistilled gasolene (86° Bé). The soap solution is thrown away. The gasolene solution is concentrated to about one-half its volume

---

[1] J. Am. Chem. Soc., **32**, 1071 (1910). [2] Ibid., **26**, 665 (1904).

and washed with warm water mixed with a little alcohol in the separatory funnel until all the soap is removed. The remainder of the gasolene is distilled off in the water-bath, and the residue heated to 130° C. in a porcelain dish to drive off the water and last traces of gasolene.

From the saponification numbers of the different oils, the requisite amount of alcoholic potash is calculated, and 100 per cent. excess employed. After the saponification, when gasolene was first added and the mixture thoroughly shaken, no separation into two layers occurred, even after several hours' standing. Salt was added, but without effect. Finally water was added in small quantities until two distinct layers formed. In washing the gasolene solution water alone was tried, but did not appreciably dissolve the soap. When warm water, mixed with a little alcohol, was used the soap dissolved readily. In heating the oil to 130° C. to drive off water, a very small flame or, better, an electric stove should be used, and the oil constantly stirred to prevent bumping. A thermometer serves well as a stirring rod.

The unsaponifiable oil is freed from cholesterol and other higher alcohols by boiling for an hour with 100 cc. of acetic anhydride in a flask provided with a return flow condenser, and heated over a sand-bath. Water is added, and the solution transferred to a separatory funnel, where it is washed with water and alcohol until the upper layer is clear and no odor of acetic acid is perceptible. The cholesterol and higher alcohols are dissolved by the acetic anhydride, leaving the hydrocarbons.

After submitting the oils to this process, a determination of their saponification number is made, and if more than 0.2 cc. of alcoholic potash is used up, the treatment with alcoholic potash and acetic anhydride repeated.

The examination of distilled wool grease is conducted upon the same general lines as indicated in the case of wool fat. Lewkowitsch[1] obtained the following results:

Free fatty acids	54.9 per cent.
Combined fatty acids, glycerides	7.0 " "
Unsaponifiable matter	38.8 " "

Some distilled grease oleines analyzed by the author showed the following composition:

Free fatty acids (oleic)	37%	47%	52%	37%
Glycerides	33%	3%	18%	18%
Unsaponifiable matter	30%	51%	30%	45%
Flash point, °F	364°	360°	370°	346°

Adulterants.—The only adulterant is mineral oil, the detection of which has already been given.

Uses.—Distilled grease stearine is used in soap and candle making; the oleine is used as a "wool oil."

Sod Oil, Moellon, French Degras.—This is an oil obtained as a by-product in the process of currying leather, or specially prepared.

Preparation.—The skins after being dehaired are well rubbed with fish oil, either "cod," whale,

---

[1] J. Soc. Chem. Ind., **11**, 141 (1892).

or menhaden, and thoroughly stuffed with the oil in the "stocks." They are then piled in heaps, whereby a kind of fermentation or "heating" ensues, care being taken that the temperature does not rise too high, the process being complete when the leather assumes the well-known yellow color of chamois leather. It is well scraped with a blunt knife, washed with soda or potash, the emulsion treated with acid, and the oil which rises to the surface is added to that obtained by scraping.

Properties.—It is a light or dark brown oil of peculiar odor, betraying its origin.

Composition.—Prepared in the way indicated, its composition must naturally be very varied; besides unchanged oil and free fatty acids, it contains a resinous substance or "degras-former," probably a mixture of oxidized oils and their anhydrides. Jean[1] states that this is soluble in alcohol and ether, insoluble in petroleum spirit, and is saponifiable, but the soap is not precipitable by salt. Moellon also contains unsaponifiable matter coming from the oils used in its preparation.

The following shows the results of the examination of 12 sod oils found on the American market by Hopkins, Coburn, and Spiller.[2] The results are calculated in per cent. on the water-free oil and the acids in milligrams of KOH per gram of oil.

---

[1] Mon. sci., **15** (1889).

[2] J. Am. Chem. Soc., **21**, 291 (1899).

	Water.	Ash.	Mineral Acid.	Oil, etc., sol. in Pet. Ether.	Soap, etc., sol. in Alcohol.	Hide Fragments.	Unsap. Matter.	Oxidized Acids.	Free Fatty Acids.
Minimum.	1.0	0.05	1.1	56.6	0.7	0.15	0.4	1.1	32.6
Maximum.	40.6	1.0	91.5	96.6	8.8	3.0	42.6	26.4	34.3

Examination and Adulterants.—The determinations to be made upon sod oil are indicated above; that of water is effected by mixing five grams of the sample with sand until a solid mass is obtained and drying at 110° C. It usually contains unchanged oil which is added to it after its formation, this cannot properly be regarded as an adulteration. Mineral and rosin oils may sometimes be found in it, obviously added with fraudulent intent. The specific gravity of the water-free degras is higher than that of the oils from which it is made; it varies from 0.945 to 0.955, and if it be as low as 0.920 an admixture with mineral oil is indicated.

Uses.—It is used for currying leather.

Oil Foots.—*Preparation.*—The term "foots" is applied by the oil and paint trade to any sediment obtained in the manufacturing or storing process. It is a mixture of oil, the impurities contained in the oil coming from the seed, or "mucilage," as it is called, coloring matter, water, dirt, and where alkali has been used in the refining process, of the saponified oil or soap.

Properties.—Cotton-seed oil foots[1] or soap-stock varies in color from light, dirty yellow, through

---

[1] Wesson, J. Soc. Chem. Ind., **26**, 595 (1907).

dark green to deep red, changing to black on exposure to the air. The odor is that of decomposed fish, due probably to methyl amine. If it contains more than 40 per cent. of water it ferments easily in hot weather and the soap made therefrom is poorer in color than that made from the fresh stock.

Composition and Analysis.—This has been given under preparation; it varies with the amount and strength of the alkalies used: the total fatty acids vary from 35 to 65 per cent., 45 being a fair average; less than 40 per cent. cannot be delivered on contracts. The specific gravity is from 0.97 to 1.04, 1.00 being the average.

A typical analysis is as follows:

Water	36.0
Fatty anhydrides	48.5
Glycerine	4.0
Caustic soda, Na_2O	3.2
Color	2.4
Organic matter	5.8

Uses.—It is used for the manufacture of soap, textile or mill soaps particularly, and is by far the cheapest soap-making material on the market. Many of the "washing powders" are composed of settled foots soap and soda ash. In England the foots are distilled with superheated steam after the manner of wool grease, which has already been described: an oleine, stearine, and cotton-seed stearine pitch are the products. Other foots beside cottonseed are linseed, whale, sperm, and olive oil.

Fuller's Grease.—"Seek oil" (England), Recovered Oil.

Preparation.—This is obtained from the water in which woolen cloth has been washed, by a process exactly similar to that by which wool fat is produced. It consists, therefore, of the oil which has been used in carding and spinning the wool, together with the fatty acids obtained from the scouring soap used, and those which existed in the oils as such. Olive, lard, neat's-foot, saponified, and distilled red, or "elaine oils," "distilled grease," oleines and mineral oils, sometimes mixed with wool fat or degras, are some of the oils used for this purpose, or "wool oils."

Composition.—This will vary according to the oils and soaps used, and the results obtained should be compared with the constants of the oils originally employed. If the oil is to be used again as a wool oil the spontaneous combustion and saponification tests should be applied.

Black Oil.—This is the term applied to oil extracted from the greasy waste of woolen mills and is, except for mineral oil coming from the machinery, the same as that upon the wool itself. It should not be confounded with a petroleum product, black oil, a crude petroleum from which naphtha and burning oil have been distilled and used for freight-car lubrication.

Garbage Grease.—This is a grease obtained by the extraction of garbage with naphtha or carbon tetrachloride. It is used for the manufacture of cheap toilet soaps, or distilled as is wool fat.

Lubricating Greases.—Gillett[1] divides the greases into six classes:

1. The tallow type, a mixture of tallow with palm oil soap with some mineral oil; this was common twenty years ago.

2. The soap thickened mineral oil type, a mixture of mineral oil usually with lime or sometimes soda soaps, the commonest type at present.

3. Types 1 or 2 mixed with graphite, talc, or mica.

4. The rosin oil type: a mixture of rosin oil thickened with lime, or sometimes litharge, with mineral oil. They contain often 20 to 30 per cent. of water and are used as gear greases. They may contain also tar, pitch, ground wood, or cork, and any of the fillers mentioned in 3.

5. Non-fluid oils: oils or thin greases stiffened with "oil pulp" or "dope," *i.e.*, aluminum oleate.

6. Special greases with special fillers.

These greases show a high coefficient of friction at first, causing a rise of temperature which melts the grease—producing the effect of an oil-lubricated bearing. The graphite greases showed an unexpectedly low lubricating power; the rosin greases showed a high friction at first but, after the bearing had warmed up, compared well with the more expensive greases. The high moisture content would seem to have the advantage of making them less sticky. The lime-soap greases (Class 2) are not as good as the tallow greases (Class 1), and are inferior as lubricants to those mixed with soda soaps.

---

[1] Jour. Ind. and Eng. Chem., **1**, 357 (1909).

By choosing the materials, soft or hard soaps, and light medium or heavy oils, or solid greases, with suitable fillers—talc or graphite—and varying their proportions, greases can be made in any desired consistency, from the semi-fluid oil to the hot neck grease.

Greases are in many cases to be preferred to oils, particularly where oil spots from the bearings are to be avoided; the most fluid grease that will stay in place and do the work should be chosen as with oils. They are used upon dynamos, shafting, gears, and where heavy pressure is applied, as in the trains of rolls in rolling mills. Some of these greases have received special names, as Fibre Grease, Gear or Pinion Grease, Graphite Grease, Petroleum Grease and Hot Neck Grease.

Fibre Grease is so called because it appears to be fibrous, especially when pulled apart; it is an anhydrous soda or potash soap (Class I) mixed with mineral oil. *Gear Grease* is usually a mixture of fibre grease with mineral oil, or it may contain rosin oil (Class 4). *Pinion Grease* is commonly made from petroleum residuum (still bottoms); pine tar is often added, and in some cases the grease consists solely of this tar, to the detriment of its lubricating qualities. *Graphite Grease* is a mixture of about one part graphite and two parts gear grease; it is especially useful in wet places, as it is not easily washed out of the bearings, particularly if it be compounded with a lime soap. *Petroleum Grease* is a heavy vaseline-like body obtained from still residues (Chapter

V) after the cylinder oil has been distilled off. *Hot Neck* Grease is the stiffest of all the greases; it is usually a stearine or wool grease pitch, or petroleum residuum mixed with rosin talc and graphite. The tests applied to greases are much the same as those applied to the oils modified as the differences (in composition and) between the solid and liquid state require.

The following tests are usually applied to the greases: flash, free acid, dropping point, soap content, free oil or fat, saponifiable and mineral, free lime, fillers and water.

For the flash point a 50 cc. porcelain crucible is used; the free acid is determined as with the oils; the dropping point according to Ubbelohde's method, by noting the temperature at which drops fall from a tube of grease surrounding the thermometer and having a standard orifice at the bottom. The soap content is most readily determined by ashing the grease and applying the usual quantitative methods to the ash. The free oil or fat is determined by extraction with gasoline, or if lime soaps be present, with ethyl acetate at room temperature; the oils extracted are examined as described under oils; the free lime and fillers are determined by the usual quantitative methods. Water is best determined by distilling with xylol according to Marcusson.[1] The following table shows the composition of some of the greases:

Grease or "Cup Grease" should be homogeneous, and contain at least 80 per cent. mineral oil of 24°–

---

[1] Mitt. k. Materials prufungs Amt., **24**, 48.

*Composition of Some Greases.**

Name.	Flash pt. °C.	Mlt. pt. °C.	Consistance Grams 20°C.	Water.	Ca. soap.	Filler.	Min. oil.	Fatty oil.	Free acid.	Coeff. friction.
Graphite	195	93	18	tr.	11	16	56	17	0	.097
Summer motor	160	87	170	tr.	38	..	36.5	25	tr.	.075
Winter motor	175	86	7	tr.	23	..	40	37[5]	6.1	.063
K_1	193	85	24	0.2	16	..	67	16	0	.057
K_2	195	93	66	0.3	20	..	60	20	0.3	.054
Auto	190	79	11	1.0	19	..	60	20	tr.	.046
Tallow	210	52	150†	2.5	..	1.4[1] 2.1[1]	22	73.5	0	.022
Tallow xx	215	49	200	tr.	..	30[7]	20	48	0	.029
Lead resin oil	240	102	7	24.7	..	1.7[2]	..	0	0	.067
Lime resin oil	198	77	31	tr.	..	9.9[3]	..	0	0	.048
Lime resin oil	198	75	4	20.0	..	7.8[3]	..	0	0	.036
Soda grease	215	83	35	0	..	22[4]	78[6]	0	0	.019
Non-fluid oil	210	76	27	0	9.8	12.9[4]	70.3	7	0	.026
No. 4 Petrolatum	247	47	6	0	..	..	100	–0	0	.018
Lard oil	265	5	0	0	..	..	0	100	..	.011

† Estimated [1] Potash soap. [2] Lead soap. [3] CaO. [4] Soda soap. [5] Mainly palm oil. [6] Oil of 24.2° Be. [7] Paraffine.

* Gillett, *loc. cit.*

28° Bé.; it should be neutral—containing neither free alkali nor fatty acids, nor should it contain grit nor useless filler, as paraffine wax. The ash should not exceed 2.75 per cent. and the loss or evaporation for an hour at 110° should not exceed 3 per cent.

Miscellaneous Oils.—*Automobile* or *Gas Engine Oils.*—Gas engine oils, particularly for the cylinders, should possess as their chief requisite, besides that of lubrication, the property of not carbonizing at the temperatures attained. The liability of carbonization seems to be intimately connected with the amount of tarry matter yielded in the gumming test and residue in the carbon residue test. For automobiles,[1] oils of the following characteristics have yielded good results: Flash 400°–470° F, viscosity 180–185 at 100° F., gumming tests very slight or slight. For large size gas engines, probably a heavier oil would be required, having these characteristics.[2] Gravity 26–28° Bé., flash 400–475° F., viscosity 250 seconds at 100° F.

Belt Oils or Dressing.—Where the object is the softening of the belt they are usually mixtures of solid fat, waxes, degras or acidless tallow (70 per cent.) with castor or fish oils (30 per cent.) to make the belts cling; in some cases they are mixtures either of corn or cotton-seed oils which have been treated with sulphur chloride, with mineral oil and thinned with naptha, or they may be mixtures of the above fats with rosin or rosin oil. These latter are less desirable. Preparations containing wood tar are also used.

---

[1] See Appendix p. 214.

[2] Davis, "Friction and Lubrication," p. 121.

Car Oils, Reduced Oils, Well Oil, Black Oils.—These are commonly crude oils from which the more volatile portions, the napthas and burning oils, have been removed by distillation or sunning. Some railroad specifications require a gravity of 29° Bé., flash-point 280°–300° F., cold test 10° to 32° F., according to the season of use and a viscosity 160 to 220 at 130° F. The lower figures refer to the "Summer," the higher to the "Winter" oils.

Compressor and Ice Machine Oils.—These are light spindle oils of a gravity of 31°–33° Bé.[1] The cold test should be 0° to 4° F. They should have a low evaporation test and a flash point at least 100° F. higher than the highest temperature likely to occur in the cylinders. A filtered oil should be used, and for pressures up to 125 lbs. per square inch, it should have a viscosity of 270 at 100° F.; for high pressures an oil of 320 or even higher viscosity at 100° F. should be used.

Crank Case Oils.—These should emulsify but little with water, consequently should be pure filtered mineral oils and not acid treated. Much seems to depend upon the water with which the oil is mixed in the crank case, so it is difficult to predict how oils of practically the same constants will behave with different waters. An oil giving these figures has proved eminently satisfactory, gravity 26°–27° Bé., flash 455° F., viscosity 100 at 212° F.

Cylinder Oils.[2]—These are divided into low and high pressure: the problem to be met consists in

---

[1] Flpt. (=Flashpoint) 375°–390°, Visc, (=Viscosity) 140″–150″ C., 100° F. Callan, Power, 48, 229.

[2] See also an excellent article by Fairbanks Power 42, 805 (1915).

making the oil adhere to the surfaces of the piston and valves. This is accomplished by the addition of some fatty oil which adheres to the metal and the mineral oil adheres to it. The action of the fatty oils would seem to be analogous to that of a mordant in fixing dyes. Pure fatty oils while they have been, and may now in some cases (with low pressures) be used, are open to the objection that these, being glycerides, are decomposed by high-pressure steam with the liberation of fatty acids which attack the iron of the cylinder, causing pitting and scoring.

$$C_3H_5(St^1)_3 + 3H_2O = C_3H_5(OH)_3 + 3HSt$$

On the other hand, when the condensed water from the exhaust steam is used as boiler-feed water, owing to the fact that these fatty oils emulsify so well with it, renders it necessary to use pure mineral oils. The cylinder stocks, that is, the pure petroleum bases, have the following characteristics: Gravity 23–28° Bé., flash 500–630° F., viscosity 100–230 at 212° F. For superheated steam, the following figures are given for the oil to be used: flash point 625–640° F., viscosity 315–325 at 212° F. The fatty oils used have already been mentioned (p. 91) and vary in quantity from 1 to 25 per cent.; the wetter the steam, the larger the amount of compounding.

Dressing Oils.—See p. 177.

Engine Oils.—Engine oils are classed as light and heavy (p. 91): a heavy oil has a viscosity of 280–340 seconds at 100° F.; medium 175–200 and lights 50 to 150 seconds at 100° F. Besides being used for engines they find general employment about

---

[1] St = Stearic acid $C_7H_{35}COOH$.

the mill or works. Where the duty is heavy or the bearings are rough, they are sometimes mixed with animal oils, as lard or whale.

For Diesel Engines[1] special oils are required as follows: for high speed marine engines, a neutral, filtered oil of 150 seconds' viscosity at 100° F. for heavier engines, a filtered cylinder stock of 150 viscosity at 212° F.; for heavy and slow speed engines, an oil of 450 viscosity at 100° F.

Marine Engine Oils have about the following characteristics: gravity 22°–24° Bé., viscosity 350–580 seconds at 100° F.; flash 395–470° F. These are usually compounded with as much as 15 per cent. of extra No. 1. lard, or 25 per cent. of blown rape oil to give them lathering properties in contact with water. Experience has shown that the addition of these organic oils is unnecessary; they are expensive and gum the wick feed.

Milling Machine or Soluble Oils.—These are usually lard, sulphonated fatty or minerals oils, or mineral oils held in suspension by soaps or alkalies, as borax, sodium carbonate; the soaps are either ammonium, sodium or potassium, with oleic, resin or sulpho-fatty acids. They should not appreciably attack the metals and should form a persistent emulsion. The U. S. Navy requirements are that upon 24 hours' standing upon polished brass or copper, it must not be turned green; German requirements are that a steel plate 30 x 30 x 3 mm. should not lose more than 18 mg. in a 1 or 2 per cent. solution of the oil after lying for three weeks in it.

Neutral Oil.[1]—An oil without "cast" or "bloom," obtained by sunning in shallow tanks. The term was formerly applied to oils of 32°–36° Bé., 290°–318° F., flash, and 47–81 seconds' viscosity at 70° F. At present the term includes "viscous neutrals," of a viscosity above 135 seconds at 100° F. and "non-viscous neutrals" below this figure.

"Oil-Dag."—This is the term applied by Acheson, the discoverer and maker of carborundum and artificial graphite, to a colloidal suspension of pure deflocculated graphite in oil, so fine that it will go through the finest filter paper. Care must be taken that the oil is free from acid, whether mineral or organic, as this causes a precipitation of the graphite.

Oilless Bearings.—These are wooden blocks often of maple, thoroughly impregnated with 35 to 40 per cent. of grease, which replace metal journals; the grease may be a mixture of paraffine, myrtle or beeswax with stearine, tallow or vaseline.

Screw Cutting Oils.—These are often mixtures of 26°–29° Bé. paraffine and 25 to 30 per cent. fatty oil, preferably cotton-seed, although lard and whale are sometimes used.

Textile Machinery Oils.—These are spindle oils, loom oils and the various kinds of engine oils.

(a) *Loom Oil.*—This is merely a heavy spindle oil: one which the author tested had a gravity of 28°, flash 360° F., and viscosity of 203 seconds. Here,

---

[1] **Battle, "Industrial Oil Engineering," p. 186.**

as in the case of the spindle oils, the evaporation test should be low, as the hydrocarbon vapors formed have occasioned serious fires.

(b) *Spindle Oil.*—This is the lighter and most fluid of the lubricating oils: the gravity varies from 27–35° Bé., the flash from 320° to 430° F., the viscosity 30–400 seconds at 70° F., and the evaporation test should not be over 4 per cent. From what has already been said (Chapter IV) nowhere is the necessity for low viscosity greater than in the case of these spindle oils when the bearings are multiplied by thousands. A case is on record where the increase in the viscosity of the spindle oil stopped the engine and shut down the mill. Besides being used for spindles, it is used for sewing machines, typewriters, etc. For bath spindles, the viscosity may be 95 to 100 seconds at 100° F.; for open spindles, this may be increased to 140 or 150 seconds.

(c) *Stainless oils* are spindle or loom oils mixed with fatty oils, lard or neatsfoot: the fatty oil being more easily emulsified or possibly saponified, in the scouring process aids materially in washing out the mineral oil with which it is mixed. One type of these oils is compounded of 40 per cent. neutral oil, 30 per cent. cotton-seed, 20 per cent. olive and 10 per cent. first pressing castor.

Transformer Oils.—These should be either pure rosin or mineral oils and be free from water, acid, alkali and sulphur. They may be freed from the first two impurities by treatment with sodium wire or from water, also by calcium chloride, after the usual method of organic chemistry.

They should not lose more than 2.2 per cent. when exposed to 190° F. for 8 hours, have a viscosity of about 400 seconds at 70° F., a flash of 340°–380° F. and remain liquid at 32° F.

Turbine Oil.—Steam turbines require a pure filtered, non-emulsifiable, mineral oil of excellent quality—free from acid and tendency to resinify and low in sulphur: as the oil is circulated around the bearings by a pump it should be of low viscosity and gravity, and free from mechanical impurities. An oil of 29–31 Bé., 145–180 seconds' viscosity at 100° F. and 390 to 420° flash has given good results.

Watch Oil.—For oiling the most delicate machinery, as watches (and clocks), the oil obtained from the dolphin, blackfish or "snuffer" is used. This exists in the cavities of the jaw, and also in the brain or "melon" of the fish; it is rendered at a low heat, chilled and filtered at a low temperature, bleached and refined by sunning in contact with lead plates to remove acid. It is a pale yellow, very fluid oil of peculiar odor; the viscosity is about 100 seconds at 100° F.

Wool Oils.—The various oils used in oiling wool have been mentioned under Fuller's Grease (p. 159). A wool oil should be examined for flash-point, unsaponifiable matter, for fatty acids, the extent to which it will gum on exposure to the air, and liability to occasion spontaneous combustion.

The liability to gum on exposure to the air can best be determined with the apparatus of Richard and Hanson.[1]

This enables a current of air to be drawn over the oil, which is exposed in a thin layer at a temperature of 400° F. for two hours: the extent to which the oil gums is measured by noting the percentage increase in its viscosity; an oil showing an increase of over 8 per cent. is liable to give trouble. The method has been tested by Richardson & Jaffe,[2] and also by the author and found to give reliable results.

Finally in making out specifications, certain mechanical details should not be overlooked. The barrels should be clean and the oil should be free from specks, dirt, stearine, glue or anything likely to clog the lubricators that may be used; the oil should be free from tar (still bottoms) as shown by the gasoline test, and if compounded should be composed of oils that mix perfectly.

Edible Fats.—These include butter, lard and hardened oils.

Butter is examined for water, fat, ash, curd, and salt; these are usually present in the following proportions:

	Per cent.	Average per cent.
Fat	78. –90.	82
Water	5. –20.	12
Salt	0.4–15.	5
Curd	0.1– 5.	1

These are determined as follows: weigh about 2

---

[1] J. Soc. Chem. Ind., 24, 315.

[2] Ibid, 534.

grams of butter into a platinum Gooch crucible half filled with ignited fibrous asbestos, and dry it at 100° C. to constant weight. The loss is the amount of *water*. Dissolve out the fat by repeated treatment with petroleum ether and again dry to constant weight. The loss represents the amount of *fat*. Ignite the crucible with a low flame or in a muffle, being careful not to volatilize the salt, until a light-gray ash is obtained. The loss represents *curd* and the residue *ash*. By extraction of the ash with water, and neutralization with calcium carbonate, the salt can be titrated with silver nitrate.

Examination of the Fat.—Butter is adulterated with oleomargarine, renovated butter, and cocoanut oil. The first may be detected by testing for cottonseed or sesamé oil either by the color tests or by the index of refraction; this at 25° is for butter 1.459–1.462, for oleo. 1.465–1.470. Owing to the fact that butter contains a large per cent. of volatile fatty acids (butyric, caproic, caprylic and capric acids, in all about 8 per cent.), adulterants may be detected by determining the amount of these. The process usually employed is that of Reichert modified by Meissl.

Five grams of the clear fat, filtered through absorbent cotton, are weighed into a 250-cc. round-bottomed flask and saponified by 2 cc. potassium hydroxide 1 : 1 and 10 cc. of 95 per cent. alcohol, under a return flow condenser for twenty-five minutes. The alcohol is rapidly evaporated off on the water bath until no odor of alcohol is perceptible. Add slowly

160 cc. of recently boiled distilled water which has been cooled to 50° or 60°; warm the flask until a clear solution of the soap is obtained. Cool to about 60° and add 8 cc. sulphuric acid 1 : 4 to liberate the fatty acids. Drop into the flask two bits of pumice (about the size of peas) which have been heated and quenched in water, and tie in a well-fitting cork; warm the flask until the fatty acids have melted and are floating on the liquid. Cool to about 60° and attach the flask to a condenser, using a trap to prevent the sulphuric acid from being mechanically carried over; 110 cc. are distilled into a graduated flask in as nearly thirty minutes as possible. Thoroughly mix the distillate, pour through a dry filter, and titrate 100 cc. with $\frac{N}{10}$ NaOH, using phenolphthalein as an indicator. Multiply the cc. of alkali by 1.1 and calculate them to 5 grams of fat. The Reichert-Meissl value for butter is from 24 to 34, the average is about 28.8; cocoanut oil gives 6–8 and other fats less than 1.

The procedure is a conventional one and should be followed as exactly as possible. Cocoanut and other vegetable oils would be shown by the fact that the unsaponifiable matter would contain phytosterol; also by the Polenske number.[1] Renovated butter is best shown by the "Spoon or Foam Test." This consists in melting a third of a teaspoonful of the sample in a tablespoon over a small flame and stirring with a match. Increase the heat until the fat boils briskly, stirring thoroughly several times. Oleo-

---

[1] Z. Nahr. Genussm., **7** 193, 1904, also Leach, "Food Analysis."

margarine and renovated butter boil noisily, sputtering like a mixture of grease and water and produce no foam. Butter boils with less noise and much foam, sometimes rising over the sides of the spoon. The pieces of curd in butter are much smaller than in either of the others.

Preservatives.—Benzoic, boric and salicylic acids, may be examined, according to the procedure given in Woodman and Norton, "Air, Water and Food," pp. 154 and 196.

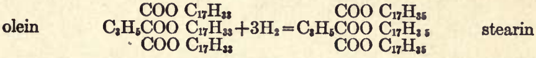
Color may be detected according to Allen, "Commercial Organic Analysis," 4th Ed., Vol. II, or Leach's "Food Analysis."

Lard is adulterated with water, 25 per cent. being added in some cases, with cotton-seed oil or stearine and beef stearine.

Water is determined as with butter; *cotton-seed oil* or stearine by the usual tests. It should be borne in mind, however, that hogs fed on cotton-seed meal yield a lard which will give the Halphen test as strongly as if it contained 25 per cent. of the oil. The iodine number and the presence of phytosterol will confirm this test; the iodine number varies widely according to the source of the fat, but in general, it may be said it should be between 46 and 66.

Beef stearine is very difficult if not impossible of detection. For this, reference may be had to Lewkowitsch, 5th Ed., Vol. II.

Hardened Oils.—As the name denotes, these are oils which have been changed to more or less solid fats by the addition of hydrogen, in the presence of a catalyst. The addition of three molecules of hydrogen to olein, a mere trifle of a tenth of an ounce, or a cubic foot to the pound, being sufficient to change it to stearin.



$$\text{olein}\quad C_3H_5\begin{matrix}COO\ C_{17}H_{33}\\ COO\ C_{17}H_{33}\\ COO\ C_{17}H_{33}\end{matrix}+3H_2=C_3H_5\begin{matrix}COO\ C_{17}H_{35}\\ COO\ C_{17}H_{35}\\ COO\ C_{17}H_{35}\end{matrix}\quad\text{stearin}$$

The procedures previously followed, by reduction of "red oil" with hydriodic acid, by chlorination and subsequent reduction with zinc, by reduction with nascent hydrogen, by treatment with electricity in an atmosphere of hydrogen, were all either too expensive or gave indifferent yields.

In 1905 Sabatier and Senderens[1] called attention to the fact that hydrogen could be added to unsaturated bodies by the use of finely divided nickel, cobalt, iron or copper, at a temperature of about 300°.

As carried out at the present time, the process consists in causing the oil to circulate through grids supporting the catalyst, usually nickel or palladium, at a temperature of about 180–250° C., and under a pressure of ninety pounds of hydrogen. The melting point of the fatty acids ("Titer" or "Titer Test") is raised, and the operation can be interrupted at any point to give a fat of the desired consistency. As a result any oil, cotton-seed, linseed, whale or fish, garbage grease, whether ancient or recent, sweet or strong-smelling, can be transformed into soap or candle stock of any desired hardness. The

---

[1] Annales d. Chim. et Phys. [8] 4, 335.

process does even more than this, it changes the before-mentioned oils—an ancient fish oil for example—into edible fats: the product is bacteria-free and physiologically uninjurious. So successful has the process become, that it is proposed to limit by law the production of edible fats and oils from loathsome sources; for example, garbage grease, cadaver and by-product fats. While it might be easy to pass this law, its enforcement would be extremely difficult, as the recognition of the different fats and oils now is well-nigh impossible; the difficulty of recognizing them after having gone through this process would probably be unsurmountable.

They do, however, contain nickel; not as much as fats take up when cooked in nickel or nickeled dishes, and need cause no apprehension.

Test for Nickel.[1]—10 grams of the fat are heated as the water bath with 10 cc. of hydrochloric acid (Sp. Gr. 1.12) with frequent shaking for two or three hours. The fat is removed by filtering through a wet filter, receiving the filtrate in a porcelain dish; after partial evaporation of the filtrate, 2 or 3 cc. of strong nitric acid are added and the evaporation continued to dryness to ensure the destruction of the organic matter. The residue is dissolved in a few cc. of distilled water, a few drops of a 1 per cent. solution of dimethyl glyoxime in alcohol added, and a few drops of dilute ammonia. The presence of nickel is shown by the appearance of the red colored

---

[1] Kerr. J. Ind. And Eng. Chem., **6**, 207 (1914).

nickel dimethyl glyoxime. The amount of nickel can be determined colorimetrically.

They are employed as soap stock—a fish oil which it would have been utterly out of the question to use, on account of the odor and consistency of the product, now gives a soap which has a "finer, cleaner and whiter look than that made without it." The slight odor can be masked by perfume. A disadvantage of the use of these fats is that the soap is so hard that it lathers poorly.

They find wide use as edible fats.

It is claimed for them that they can be heated hotter (to 455° F.) without smoking than ordinary fat: this cooks the outside of the food more quickly and prevents the grease from soaking in. Consequently it is less greasy, more digestible, dry and crisp. Another advantage is that no odor is absorbed by the fat. Another claim is that one-fourth less is used of these fats than of butter; further that it is all fat, while butter contains 5 to 16 per cent. of water.

Finally hydrogenated vegetable oils seem to offer a satisfactory substitute for animal fats to those who object to the latter from prejudice or religious scruples.

Dressing or finishing oils are either distilled grease, oleines or soluble oils, which are applied to the woven goods to soften them and produce a softer finish.

References.—"The Hydrogenation of Oils," Ellis, 1914.
The Hydrogenation of Oils, Moore, J. Ind. and Eng. Chem., 9, (1917), 451.

Cutting oils[1] are divided into two classes, straight and soluble.

Straight is lard oil for fine and delicate work, special steels etc., except where the heat generated is high. Lard oil adheres better to the point of the tool than any other oil. Free fatty acid should preferably be absent. It is mixed with other oils, lardoleum, mineralized lard oil, etc. Oil should have moderately high viscosity, excellent heat conductivity, high flash, low cold test; should be free running, non corrosive, must not thicken or gum. There should not be over 5% free acid in lard oil. No phenolic or other disinfectants in it on account of effect on the workmen; efficiency according to the amount of lard oil.

Soluble.—These form milky emulsions with water; used for heat conduction in heavy cutting, milling, stamping, etc. Sal soda solution originally used; they are usually mineral oil and treated animal or vegetable oil, as lard, cottonseed, corn, rape, castor, olive, rosin, neatsfoot and others. Called sulphonated, phenolated or soap oils.

Sulphonated oils are made by treating the oils just mentioned with sulphuric acid, washing with brine, neutralizing with ammonia or alkali in excess. May cause trouble by the content of free sulphuric acid.

Soap Oils are soluble oils containing soap. Mix mineral oil with animal or vegetable and partly or wholly saponify. When water is added a creamy

---

[1] Condensed from an article by Copeland, Met. and Chem., Eng., **17,** 25 (1918).

emulsion is formed. Alcohol is sometimes added. Excessive soap is to be avoided, may cause gumming; up to 15% is permissible, less than 10 unusual.

Phenolated Oils. Compounded of carbolic acid and alkali; odor not objectionable nor detrimental. A good oil should be homogeneous not segregate into its various components on standing: Should form perfect emulsion with water, with minimum-separation of mineral oil. Should be made of high grade materials.

In evaluating cutting oils, consider total saponifiable matter, free fatty acids, neutral oil and soap. Stability of emulsion with various dilutions as 1:10; 1:20; separation of oil and water, may cause damage and loss of lubricating value, amount of water, volatile matter, and tendency to gum. Should not be made from rancid or inferior fats.

Analysis.—Saponify 4–6 gms. with $\frac{N}{2}$ alcoholic KOH. Boil ½ hour, evaporate alcohol, and extract soap with ether in usual way; weigh oil, acidify soap solution and extract acids with ether in usual way; weigh acids. Can also determine each fatty acid and neutral oil volumetrically, also soap determined sometimes.

Physical Tests.—Emulsification. Shake a solution 1:10 or 1:20 with water. Note character of emulsion when fresh and after standing 24 hours and segregation. Pour off top and analyze. See how it compares with original.

Evaporation.—Heat 1–2 gms. in Petri dish 50–75 mm. diameter at 100°–105° for 3 hours: heat again for 30 minutes and weigh. Light mineral oils will volatilize. Sp. Gr. Flash, Fire, Viscosity and Acid Test are also done.

Analysis of oils, see Table.

No. 1. Not recommended, on account of segregating and oxidizing properties, requires care in mixing. Fatty acid was oleic acid.

No. 2. Recommended, excellent emulsification, freedom from oxidation, thickening and gumming, for non segregation and freedom from mineral acids. Main objection considerable quantity of volatile mineral oil: contains ammonia and light mineral oil like kerosene.

No. 3. Soluble oil segregates by the settling out of the soap. Cannot be recommended on account of segregation and poor emulsification qualities. Good example of lack of skill and knowledge on the part of the maker and insufficiency of soap.

No. 4. Soluble oil, a soap oil containing alcohol: does not oxidize or thicken on exposure to the air, does not segregate, forms excellent thickening, oxidizing, gumming and for perfect emulsifying qualities.

No. 5. Sulphonated oil similar to No. 2. Consider fire hazard, contains ammonia and perhaps kerosene.

No. 6. Main defect is segregation. This is determined by dividing free fatty acids = 4.3 by mixed oil = 5.1 which gives 81.4% segregation. Emulsion good.

ANALYSIS SOLUBLE CUTTING OILS.

Oil No.	Total Sap'ble Matter.	Fatty Acid.	Free Fatty Acid.	Free Fatty Acid as Fat.	Fatty Acid as Soap.	Soap.	Neutral Oil Fatty.	Min. Oil.	Total Volatile Matter.	Alc. etc. Water, NH₃.	Price per Gal. July 1917 cents.	Emulsion 1:10 or 1:20
1[1][2]	18.7	18.3	6.2	1.0	11.2	12.1	1.3	72.1	8.3	8.3	50	fair
2[4][5]	12.9	11.9	11.4	0.2	0.2	0.3	0.4	77.6	25.3	7.0	48	excellent
3[2]	15.4	15.2	0.1	5.5	9.6	10.4	5.8	75.5	15.6	8.4	48	poor
4	16.7	16.0	4.7	3.7	7.7	8.3	4.0	76.3	....	7.0	45	excellent
5[3][4][6]	18.2	17.3	15.2	1.6	....	....	2.0	75.3	17.4[7]	3.3	44	like No. 2
6[1]	21.8	21.3	5.1	8.9	7.3	7.9	9.3	67.2	....	10.7	45	good
7	12.7	12.5	4.2	0.6	7.7	8.3	0.8	79.1	....	7.6	50	like No. 4
			Sp. Gr.	° Bé.	Flash.°	Fire.°	Viscosity.[8]					
8[2][9]	24.9	12.8	0.892	26.9	355	390	111	74.7	Straight cutting oil		45	
9	32.2	4.1	.889	27.5	396	440	192	67.6			60	
10[2][10]	11.6	3.1	.900	25.4	360	410	164	88.0			..	Dippel
11	18.9	2.1	.883	28.5	410	455	176	81.0			37	lard?

---

[1] Segregates. [2] Not to be recommended. [3] Dangerous on account of fire hazard. [4] Sulphonated oil. [5] Flash 150° F. [6] Flash 135° F. [7] Volatile mineral oil 14.1. [8] Saybolt universal at 100° F. [9] On account of low viscosity and high fatty acid. [10] On account of odor.

No. 7. Soluble oil much like No. 4.

No. 8. Should be rejected for low viscosity and excessive free fatty acid.

No. 9. Free fatty acids, moderately low flash and fire test; adequate viscosity and for good general composition.

No. 10. Saponifiable oil had a rotten odor—probably of Dippel animal oils, poor composition.

No. 11. Pure, low fatty acids, adequate viscosity, high flash and fire tests, no segregation.

APPENDIX.

TABLES, REAGENTS, AND RAILROAD SPECIFICATIONS.

TABLE I.

Requirement of Various States and Cities regarding Flash and Fire Test of Illuminating Oils.

Name.	Flash, °F.	Fire, °F.	Instrument.
Arkansas	...	130	Tagliabue.
Columbia, District of	120		
Connecticut	...	110	
Florida	...	130	Tagliabue.
Georgia	...	120	
Illinois	...	150	Tagliabue.
Indiana	120	...	Indiana.
Iowa	105	...	Elliott.
Kansas	...	110	Tagliabue.
Kentucky	...	130	
Louisiana	125	...	Tagliabue.
Maine	120	...	Tagliabue open.
Massachusetts	100	...	Tagliabue open.
Michigan	120	148	Foster.
Minnesota	110	...	Minnesota.
Missouri	...	150	Tagliabue.
Montana	110	...	
Nebraska	100	...	Foster.
New Hampshire	100	120	Tagliabue.
New Jersey	100	115	
New Mexico	...	150	
New York	...	110	Tagliabue.
North Carolina	100	...	Foster.
North Dakota	100	...	
Ohio	120	...	Foster.

Name.	Flash, °F.	Fire, °F.	Instrument.
Pennsylvania	...	110	Tagliabue.
Rhode Island	...	110	
South Dakota	110	...	Foster.
Tennessee	120	...	Open cup.
Vermont	...	110	Tagliabue.
Wisconsin	120	...	Wisconsin.

Requirements of Cities where Different from State Law.

Name.	Flash, °F.	Fire, °F.	Instrument.
Baltimore, Md	120	...	
Denver, Col	110	...	Tagliabue open.
Los Angeles, Cal	110	...	Tagliabue open.
Meriden, Conn	...	125	
Milwaukee, Wis	110	...	
Newark, N. J	...	110	
New Haven, Conn	...	110	Tagliabue open.
New Orleans, La	...	110	Tagliabue open.
New York, N. Y	100	...	Elliott.
Richmond, Va	...	110	Tagliabue.
Sacramento, Cal	110	...	Tagliabue open.
San Francisco, Cal	100	...	Tagliabue open.
Wilmington, Del	...	110	

TABLE II.

Showing the Viscosity, Flash and Fire Test of Various Oils.[1]

Name	Viscosity[2]	Flash, °C.	Flash, °F.	Fire, °C.	Fire, °F.
Castor	1485	...	505	...	...
Corn	187	249	480	335	635
Cotton-seed	180	305	582	340	644
Prime Lard	214	264	530 600	340	644
No. 2 Lard	...	215	419	242	468
Boiled Linseed	...	192	378	300	572
Raw Linseed	...	274	525	340	644
Menhaden	...	...	405	...	484
Neat's-foot	224	226	439	273	523

---

[1] Done with the apparatus described upon page 38.

[2] Seconds with Saybolt universal at 100° F.

Name	Viscosity	Flash, °C.	Flash, °F.	Fire, °C.	Fire. °F.
Olive	..	233	451	283	541
25° Paraffine	163	210	410	246	475
75% 25° Paraffine, 25% Neat's-foot	...	210	410	244	471
75% 25° Paraffine, 25% Lard	...	210	410	254	489
50% 25° Paraffine, 50% Lard	...	218	423	267	513
25% 25° Paraffine, 75% Lard	...	227	441	284	543
Porpoise (blubber)	156	...	495	...	...
Porpoise jaw	101	...	415	...	...
Rape	247	...	455	...	...
Distilled Red	...	184	364	213	415
Rosin, 4th run	228	...	257	...	...
Seal	164	...	515	...	...
Sperm No. 1	...	220	428	270	518
Sperm No. 2	115	252	486	301	574
Whale (blubber)	184	...	515	...	...

Flash Point of Certain Organic Compounds.

Name.	Flash, °C.[2]	Flash, °F.[1]	Flash, °F.[4]	Flash, °F.[3]	Fire, °F.[3]
Acetone	.....	....	34	.....	...
Denatured Alcohol	.....	....	55	50	58
Ethyl Alcohol, absolute	12	81	53	54	62
Ethyl Alcohol, + 0.5% ether	9	75	..	.....	...
Ethyl Alcohol, 4% by vol	68	181	..	.....	...
Methyl Alcohol	.....	....	45	52	56
Benzene, C_6H_6	−8	45	..	.....	...
Ether, 0.720 sp. gr., U. S. P.	—120 about				
Gasoline, 86°	—130 about				
did not flash at	—145.				
Turpentine	92–98	119–125	90	95 83–89[5]	100

---

[1] Raikow Chem. Ztg. (1899), 145: Holde and Pelgry, Chem. Centralb. (1899) **2**, 546. Done with Abel's tester and calculated to Massachusetts tester by adding 27° F.

[2] Abel tester.

[3] Done in author's laboratory with N. Y. tester.

[4] Schieffelin, J. Soc. Chem. Ind., **27**, 922 (1908), with Mass. open tester.

[5] McCandless, J. Am. Chem. Soc., **26**, 982 (1904).

TABLE III.

Relation of Baumé Degrees to Specific Gravity and the Weight of One United States Gallon at 60° F.

Baumé.	Specific Gravity.	Pounds in Gallon.	Baumé.	Specific Gravity.	Pounds in Gallon.	Baumé.	Specific Gravity.	Pounds in Gallon.	Baumé.	Specific Gravity.	Pounds in Gallon.
10	1.0000	8.33	31	0.8695	7.24	52	0.7692	6.41	73	0.6896	5.75
11	0.9929	8.27	32	0.8641	7.20	53	0.7650	6.37	74	0.6863	5.72
12	0.9859	8.21	33	0.8588	7.15	54	0.7608	6.34	75	0.6829	5.69
13	0.9790	8.16	34	0.8536	7.11	55	0.7567	6.30	76	0.6796	5.66
14	0.9722	8.10	35	0.8484	7.07	56	0.7526	6.27	77	0.6763	5.63
15	0.9655	8.04	36	0.8433	7.03	57	0.7486	6.24	78	0.6730	5.60
16	0.9589	7.99	37	0.8383	6.98	58	0.7446	6.20	79	0.6698	5.58
17	0.9523	7.93	38	0.8333	6.94	59	0.7407	6.17	80	0.6666	5.55
18	0.9459	7.88	39	0.8284	6.90	60	0.7368	6.14	81	0.6635	5.52
19	0.9395	7.83	40	0.8235	6.86	61	0.7329	6.11	82	0.6604	5.50
20	0.9333	7.78	41	0.8187	6.82	62	0.7290	6.07	83	0.6573	5.48
21	0.9271	7.72	42	0.8139	6.78	63	0.7253	6.04	84	0.6542	5.45
22	0.9210	7.67	43	0.8092	6.74	64	0.7216	6.01	85	0.6511	5.42
23	0.9150	7.62	44	0.8045	6.70	65	0.7179	5.98	86	0.6481	5.40
24	0.9090	7.57	45	0.8000	6.66	66	0.7142	5.95	87	0.6451	5.38
25	0.9032	7.53	46	0.7954	6.63	67	0.7106	5.92	88	0.6422	5.36
26	0.8974	7.48	47	0.7909	6.59	68	0.7070	5.89	89	0.6392	5.33
27	0.8917	7.43	48	0.7865	6.55	69	0.7035	5.86	90	0.6363	5.30
28	0.8860	7.38	49	0.7821	6.52	70	0.7000	5.83	95	0.6222	5.18
29	0.8805	7.34	50	0.7777	6.48	71	0.6965	5.80	..	......	....
30	0.8750	7.29	51	0.7734	6.44	72	0.6930	5.78	..	......	....

TABLE IV.

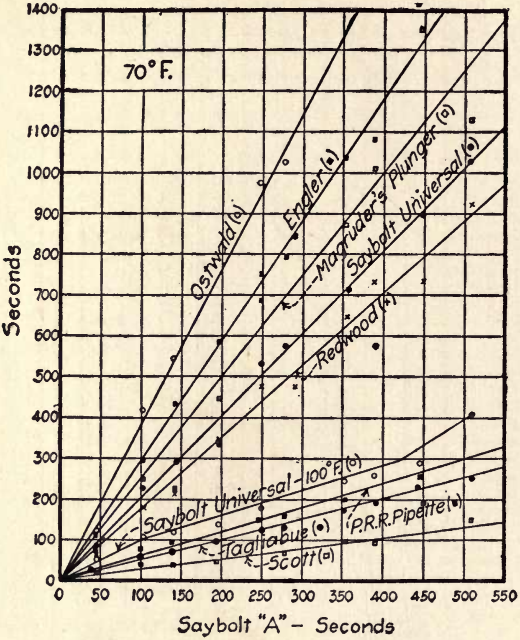
Showing the Specific Gravity, Degrees Baumé, and Weight per Gallon and per Cubic Foot of Certain Oils.

	Specific Gravity.	Degrees Baumé.	Pounds in One Gallon.	Pounds in One Cubic Foot.
Water	1.0000	10	8.33	62.50
Castor Oil	.9639	15	8.03	60.24
Linseed Oil, boiled	.9411	19	7.84	58.81
Linseed Oil, raw	.9299	21	7.75	58.12
Menhaden, light	.9325	20	7.77	58.28
Menhaden, dark	.9292	21	7.74	58.08
Hemp-seed	.9307	20	7.75	58.17
Cod Liver	.9270	21	7.72	57.94
Whale	.9254	21	7.71	57.84
Poppy-seed	.9243	21	7.70	57.77
Cotton-seed	.9220	22	7.67	57.53
Fish	.9205	22	7.67	57.53
Olive	.9192	22	7.65	57.45
Almond	.9180	23	7.65	57.38
Lard	.9175	23	7.64	57.34
Rape-seed	.9155	23	7.63	57.22
Neat's-foot	.9142	23	7.62	57.14
Colza	.9136	23	7.61	57.10
Palm	.9046	25	7.54	56.54
Sperm, natural	.8815	29	7.34	55.09
Sperm, bleached	.8813	29	7.34	55.08
Spirits of Turpentine	.8600	33	7.16	53.75
Alcohol, 90 per cent	.8228	40	6.85	51.43
Alcohol, 95 per cent	.8089	43	6.74	50.56
Alcohol, absolute	.7938	46	6.61	49.61

NOTE.—In the column marked Baumé, the nearest whole number is given, omitting fractions.

TABLE V.*

Comparison of Various Viscosimeters with the Saybolt "A" Viscosimeter at 70° F.

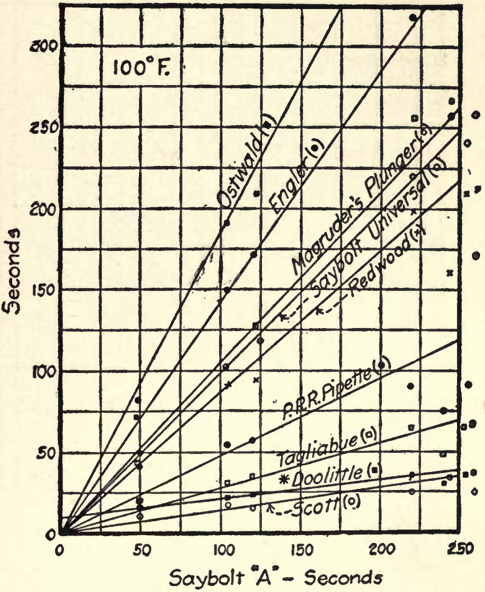


---

* This and Tables VI to VIII are taken from Proc. Am. Soc. Test Materials, 1910.

TABLE VI.*

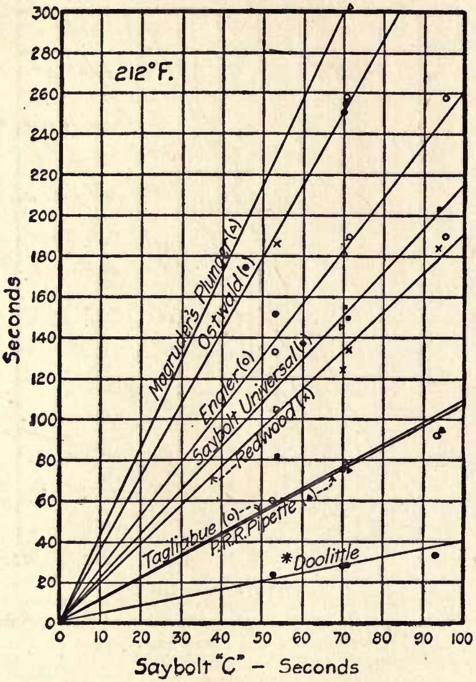
Comparison of Various Viscosimeters with the Saybolt "A" Viscosimeter at 70° F.



* The ordinates to the Doolittle curve are grams of granulated sugar, instead of seconds as with all the others.

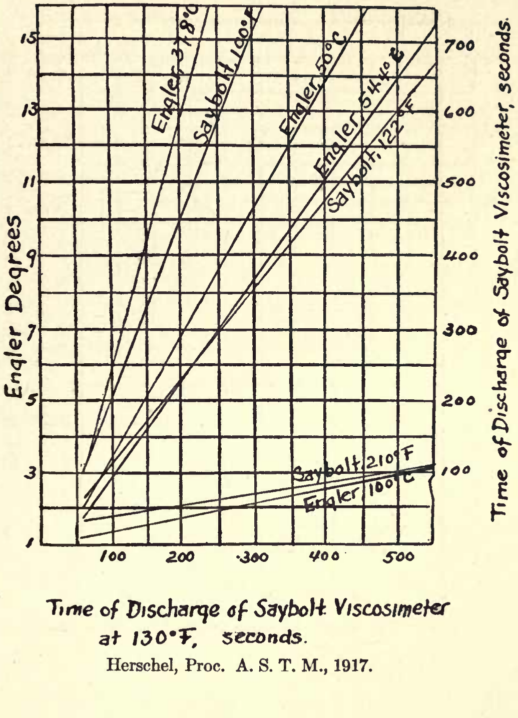
TABLE VII.*

Comparison of Various Viscosimeters with the Saybolt "C" Viscosimeter at 212° F.



* The ordinates to the Doolittle curve are grams of granulated sugar, instead of seconds as with all the others.

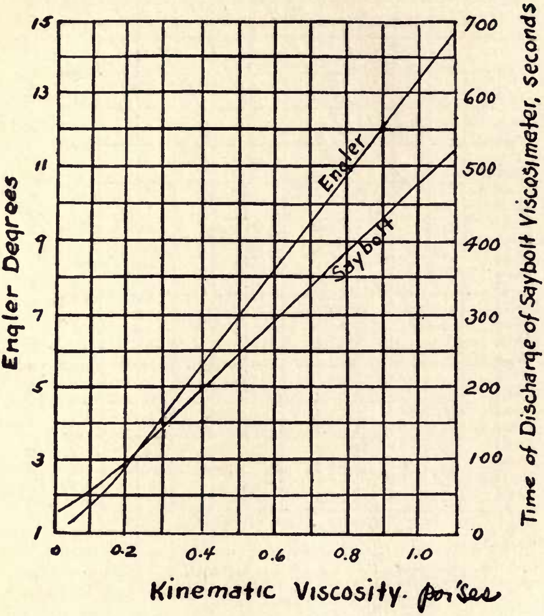
TABLE VIII*.



Herschel, Proc. A. S. T. M., 1917.

TABLE IX.

Absolute Viscosity. Engler Viscosimeter at 20° C.



Herschel Proc. A. S. T. M., 1917.

TABLE X.

Showing the Principal Characteristics of Various Oils.

NAME.	Sp. Gravity 15° C.	Valenta, ° C.	Mau., °C.	Elaidin.	Iod. per ct.	Sapon. mg. KOH.	Refractive Index, 15°–15.5° C.
Almond	.918	110	53	Solid.	97	190	1.4728
Castor	.963	Soluble.[4]	47	....	84	181	1.4795–4803
Chinese Wood	.940	40–47	...	....	163	193	1.515–.520[6]
Cocoanut	.874[1]	....	...	....	9	260	1.4573
Colza. (See Rape)							
Corn	.922	80	85	Pasty.	115	191	1.4768
Cotton-seed	.922	90[2]–110	76	Pasty.	108	193	1.4737–4757
Elain	.904	....	...	....	90[3]	200	1.4631[6]
Horse	.919	54 68 80	52	....	80	197	1.4652–1.4704[6]
Lard	.917	54 66 98	41	Very solid.	65	195	1.4694
Linseed	.934	57[2]–74 70–79	111	....	176	191	1.4835
Maize. (See Corn)							
Menhaden	.930	64[2]	126	....	154	190	1.4783[6]
Neat's-foot	.915	62 72–75	46	Solid.[5]	71	194	1.4695–4705
Olive	.916	85–111	35	Very solid.	82	194	1.4703–4713
Palm	.859	....	...	....	52	199	1.451 at 60° F.
Peanut	.917	87[2]–112	51	Solid.	98	194	1.4731
Poppy-seed	.925	....	87	....	138	193	1.4773
Rape	.916	Insoluble.	55	Pasty.	101	174	1.4720–4757
Sesamé	.923	87[2]–107	65	Pasty.	107	190	1.4748–4762
Soy Bean	.924	....	87	....	140	191	1.4680[7]
Sperm	.880	Insoluble.	46	Solid.	85	135	1.4664–4673
Sunflower	.925	....	71	....	125	192	1.4762
Tallow	.916	71–75	35	Solid.	56	197	1.4660[6]
Whale	.927	....	88	....	120	190	1.4691[6]

[1] At 99° C. [2] Allen. [3] Pure oleic acid. [4] Cold. [5] At times. [6] At 25° C. [7] At 40.°

TABLE XI.

Volumetric Factors.

1 Cc. $\frac{N}{2}$ HCl.=.018185 Gm. HCl.

1 Cc. $\frac{N}{10}$ HCl=.003637 Gm. HCl.

1 Cc. $\frac{N}{2}$ KOH=.028 Gm. KOH.

1 Cc. $\frac{N}{6}$ KOH=.047 Gm. oleic acid=.008133 Gm. H_2SO_4=.00935 Gm. KOH.

1 Cc. $\frac{N}{10}$ KOH=.0056 Gm. KOH.

1 Cc. $K_2Cr_2O_7$ 3.8633 Gm. per liter=.0038633 Gm. $K_2Cr_2O_7$=.010 Gm. I.

1 Cc. $\frac{N}{10}$ $Na_2S_2O_2+5H_2O$=.0248 Gm. $Na_2S_2O_2+5H_2O$=.01265 Gm. I.

TABLE XII.

The Action of Oils upon Metals.[1]

A. OILS.

Name.	No Action on	Least Action on	Most Action on
Cotton-seed	....	Lead.	Tin.
Lard	....	Zinc.	Copper.
Mineral	Zinc.	Brass.	Lead.
Olive	....	Tin.	Copper.
Rape	Brass and Tin.	Iron.	Copper.
Seal	....	Brass.	Copper.
Sperm	....	Brass.	Zinc.
Tallow	....	Tin.	Copper.
Whale	Tin.	Brass.	Lead.

B. METALS.

Name.	No Action on	Least Action on	Most Action on
Brass	Rape.	Seal.	Olive.
Copper	Mineral.	Sperm.	Tallow.
Iron	....	Seal.	Tallow.
Lead	....	Olive.	Whale.
Tin	Rape.	Olive.	Cotton-seed.
Zinc	Mineral.	Lard.	Sperm.

---

[1] I. J. Redwood, J. Soc. Chem. Ind., 5, 362 (1886). For the action of oil upon cement, see *id.*, 24, 970 (1905).

TABLE XIII.

Showing the Principal Characteristics of Fatty Acids derived from Various Oils.

Name.	Melting Point.	Sap. Value.	Molec. Weight.	Iodine Value.
Almond	14° C.	204	289[2]	95
Castor	13	208[2]	290–295	87–88
Cocoanut	25–27	258	200	8–9
Corn	18–21	198.4	282[2]	113–125
Cotton-seed	35–43	202–208	275–289	110–116
Horse	25–39	203	288[2]	72–87
Lard	35	204[2]	289[2]	94–95.8[3]
Linseed	17–24	197	283–307	179–209
Neat's-foot	17–26	200–206	288[2]	60–77
Olive	19–28.5	193	280–286	86–104
Palm	47–50	206	270	53
Peanut	28–33	202	282	97
Poppy-seed	20	199	282[2]	116–139
Rape	16–22	185	314	96–106
Sesamé	21–32	200	286	109–112
Soy bean	28	....	....	122
Sperm	13–21	208[2]	281–305	83–88
Sunflower	17–24	201	285[2]	124–134
Tallow	34–37	203[2]	288[2]	56
Whale	16	201[2]	293[2]	131

TABLE XIV.

Showing the Bromine Addition and Substitution Figures. McIlhiney's Method (page 67).

	Total.	Addition.	Substitution.	Iodine.
Benzine[1]	51.5	15.5	18.0	.....
Benzine[1]	6.3	2.7	1.8	.....
Cocoanut Oil	5.4	4.7	0.3	.....
Cotton-seed	65.8	62.2	1.8	.....
Corn. (See Maize.)				
Linseed, average	112.0	106.6	2.7	183.8
Linseed, boiled, average	109.5	103.0	3.2	.....
Maize, average	75.8	72.9	1.5	.....
Menhaden, average	110.6	95.6	7.5	174.9
Paraffine, hard	3.5	1.4	1.1	.....
Petroleum, neutral	14.4	6.4	4.0	.....
Rosin, w. g.	161.4	8.0	76.7	.....
Rosin, black	135.4	5.4	65.0	.....
Rosin Oil	92.3	7.7	42.3	63.9
Rosin Oil, third run	197.6	16.4	90.6	.....
Tallow	24.0	21.5	1.3	.....
Turpentine	266.1	166.1	50.0	.....

---

[1] Substitutes for turpentine. [2] Calculated. [3] Fluid acids.

TABLE XV.

Showing a Comparison of the Iodine Numbers obtained by Various Methods.

Oil.	Hübl.	Hanus.	Wijs.
Butter	35.3	35.3	36.2[2]
Castor	82.6	84.4	85.6[1]
Cod	148.5	147.5	154.6[1]
Cotton-seed	108.5	107.0	110.0[1]
Cocoanut	8.9	8.6	9.0[2]
Corn	119.9	120.2	123.2[2]
Lard	70.0	69.7	.....[2]
Linseed	179.5	183.7	188.7[2]
Oleomargarine	66.3	64.8	66.0[2]
Oleomargarine	52.5	52.0	52.9[2]
Oleomargarine	89.8	90.0	91.4[2]
Olive	79.2	80.6	79.9[2]
Peanut	96.3	97.4	99.0[2]
Poppy-seed	133.4	132.9	135.2[2]
Rape	100.2	102.8	104.1[2]
Sesamé	106.4	106.5	107.0[2]
Sunflower	106.4	107.2	109.2[2]
Whale	120.2	120.7	124.8[1]

TABLE XVI.

Formulæ to Change the Readings of One Viscosimeter Into Those of Another.

It is often desirable to change the readings of one viscosimeter into those of another at the same temperature. This can be done by means of the plots, or by the following formulæ:

Engler in terms of Saybolt A:
Up to 500″ Eng. and 160″ Say............0.32 Eng. = Say. A − 4.6
500–1200″ Eng. and 160″–370″ Say..0.32 Eng. = Say. A − 6.
Engler in terms of Saybolt C:
0.75 Eng. = Say. C + 12.5
Engler in terms of Doolittle:
Up to 400″ Eng. and 44° D...............0.1 Eng. = D. − 9.7
400″–600″ Eng. and 44°–53° D......0.07 Eng. = D. − 12.8
600–1000 Eng. and 53°–72° D.......0.06 Eng. = D. − 12.5

---

[1] Hunt, J. Soc. Chem. Ind., **21**, 454 (1902).
[2] Tolman and Munson, J. Am. Chem. Soc., **25**, 244 (1903).

Saybolt A in terms of Saybolt C:
Up to 160″ A and 365″ C.................. $A = 0.427\ C + 10$
Above 160″ A and 365″ C................. $A = \frac{C+27}{2.5}$

Saybolt A in terms of Doolittle:
Up to 133″ Say. and 44 grms. D...........0.313 Say. = D. − 8.3
133″–161″ Say. 44–48 g. D..........0.219 Say. = D. − 10.8
161″–190″ Say. 48–53 g. D..........0.233 Say. = D. − 10.4
190″–309″ Say. 53–72 g. D..........0.2 Say. = D. − 11.3
Saybolt C in terms of Doolittle:
Up to 292″ Say. and 44 grms. D..........0.133 Say. = D. − 11.4
292″–440″ Say. + 44–53 g. D ....0.093 Say. = D. − 13
440″–734″ Say. + 53–72 g. D........0.08 Say. = D. − 13.5

From the variation in various viscosimeters of the same name it cannot be expected that these formulæ will give absolutely correct results: they may be depended upon within less than five per cent.

TABLE XVII.

Absolute Viscosity of Aqueous Solutions of Glycerine in Poises.
(Dynes per square centimeter)
Compiled from researches of Archbutt & Deeley.

Sp. gr. $\frac{20^\circ\text{ C.}}{20^\circ\text{ C.}}$	Visc. 20° C. η	Sp. gr.	Visc. η	Sp. gr.	Visc. η
1.00	.01028	1.10	.03745	1.20	.4002
1.01	.01159	1.11	.04371	1.21	.5933
1.02	.01307	1.12	.05152	1.22	.9195
1.03	.01477	1.13	.06150	1.23	1.511
1.04	.01670	1.14	.07463	1.24	2.690
1.05	.01893	1.15	.09237	1.245	3.721
1.06	.02151	1.16	.1170	1.25	5.261
1.07	.02452	1.17	.1520	1.255	7.591
1.08	.02809	1.18	.2032	1.26	11.16
1.09	.03232	1.19	.2803	1.261	12.09

TABLE XVIII.

Viscosity of Sucrose Solutions in Centipoises, according to Hosking[1] & Powell.[2]

Temperature °C.	Percentage sucrose by weight.								
	1	5	10	15	20	25	30	35	40
15	1.168	1.292	1.518	....	2.212	....	....	....	7.30
20	1.031	1.139	1.328	....	1.910	....	....	....	6.07
25	0.92	1.01	1.17	1.40	1.70	2.11	2.75	3.67	5.12
30	.81	.90	1.06	1.25	1.50	1.85	2.39	3.14	4.28
50	.57	.61	.70	.80	.96	1.15	1.44	1.85	2.40
70	.41	.455	.512	....	.676	....	....	....	1.553
90	.32	.349	.389	....	.511	....	....	....	1.093

[1] Phil. Mag. 49, 274 (1900).

[2] Trans. (London) Chem. Soc. 93, 2023 (1908). Scientific Paper, 298, Bureau of Standards (1917).

Ordinary granulated sugar may be used for all practical purposes, as it is 99.85% pure, the remainder being water; it can be dried in a vacuum desiccator over sulphuric acid.

TABLE XIX.

Specific Heat of Various Oils and Fats.[1]

Oil or fat;	Sp. Heat.	Latent Heat. Btu. per lb.
Cotton-seed	.503	....
Peanut	.500	....
Soy bean	.492–.984	33–87
Cotton-seed stearine	.520	3.6
Cotton-seed hydrogenated	.76–1.515	47.–182
Peanut hydrogenated	1.16	76.5
Soy bean hydrogenated	1.50	180.
Cocoanut solid	.94	75.6
Cocoanut hydrogenated	.94	75.6
Oleo stearine	1.16	76.5

[1] Wesson & Gaylord, The Cotton Oil Press 2, 40 (1918).

REAGENTS.

The reagents used in oil analysis are few and easily obtained. A list and their method of preparation is here given.

Acetic Acid, Glacial. — Baker and Adamson's C. P., ninety-nine and five-tenths per cent. pure. The determination of its strength should be made by titration and not by specific gravity, as the ninety-eight per cent. and eighty per cent. acid have the same specific gravity, 1.067. The determination of the melting point gives results equally good with those obtained by titration and requires less time.[1] It is made after the manner of the "titer test" (p. 82), the tube being half filled, chilled to 10° or 11° C., and further chilled by placing the outside bottle in ice-water; the temperature of the super-cooled acid rises to its melting point, where it remains stationary for some time. The melting points of acids of various strengths are as follows:

100 per cent., 16.75° C.; 99.5 per cent., 15.65°; 99 per cent., 14.8°.

For Hanus's solution it must not reduce potassium bichromate and sulphuric acid.

Acetic Anhydride.—Baker and Adamson's C. P.

Alcohol.—Commercial "Cologne Spirits." For the preparation of alcohol free from aldehyde for alcoholic potash, cologne spirits are treated with silver oxide as follows: one and one-half grams of silver nitrate are dissolved in 3 cc. of water, added to one liter of alcohol and thoroughly shaken; three grams of potassium hydrate are dissolved in 15 cc. warm alcohol and, after cooling, added to the alcoholic silver nitrate and thoroughly shaken again, best in a tall bottle or cylinder. The silver oxide is allowed to settle, the clear liquid siphoned off and distilled, a few bits of pumice, prepared by igniting it and immediately quenching under water, being added to prevent bumping. Alcohol for use in the free acid determination is prepared by placing ten to fifteen grams of dry sodium carbonate in the reagent bottle, taking care to filter it before use.

Alcohol, Amyl.—Baker and Adamson's C. P.

---

[1] McIlhiney et al., J. Am. Chem., Soc., 29, 1224 (1907).

Bromine.—The commercial article; also a $\frac{N}{3}$ solution, made by dissolving 26.6 grams bromine in one liter carbon tetrachloride.

Calcium Chloride.—The dry and also the crystallized salt.

Calcium Sulphate.—Plaster of Paris.

Carbon Tetrachloride.—Baker and Adamson's C. P.

Chloroform.—Squibb's, U. S. P.

Copper.—Copper turnings or clippings, used for the generation of nitric oxide.

Copper Wire.—Cut in pieces of 0.3 to 0.5 gram.

Ether.—Squibb's, U. S. P.

Gasolene.—Gasolene, 86° Baumé.

Hydrochloric Acid, C. P.—Specific gravity 1.2. For $\frac{N}{2}$ HCl dilute thirty-nine cubic centimeters of the above acid to one liter and standardize.

Iodine Solution.—Fifty grams of iodine to one liter of alcohol. For Hanus's solution dissolve by warming 13.2 grams iodine in one liter glacial acetic acid; cool and add three cubic centimeters of bromine.

Lead, Precipitated.—Place strips of zinc in the solution of lead acetate below. When the precipitation is nearly complete the lead is washed with water, alcohol, and ether, and dried finally in a vacuum desiccator.

Lead Acetate.—One hundred grams of the salt to one liter.

Litmus Paper.

Mercuric Chloride.—Sixty grams of the salt to one liter of alcohol.

Nitric Acid.—Specific gravity 1.34.

Phenolphthalein.—One gram of the substance to five hundred cubic centimeters of alcohol.

Meta-Phosphoric Acid.—A saturated solution of the commercial "stick phosphoric acid" in absolute alcohol.

Potassium Bichromate.—Dissolve 3.8633 grams of the C. P. salt in one liter of water; one cubic centimeter is equivalent to 0.01 gram of iodine. The solution should be tested against iron wire containing a known percentage of iron.

Potassium Hydrate.—$\frac{N}{2}$: Dissolve thirty grams of "potash by alcohol" in one liter of alcohol. $\frac{N}{6}$: Dissolve ten grams of "potash by alcohol" in one liter of water and dilute to proper strength. The solution should be protected by "stick potash" from the carbon dioxide in the air. *Ten per cent.:* Dissolve one hundred grams of "stick potash" in eleven hundred cubic centimeters of alcohol.

Potassium Iodate.—A two per cent. solution.

Potassium Iodide.—One hundred grams of the commercial salt are dissolved in one liter of water. This should be free from iodate, shown by yielding no coloration when acidified with strong HCl.

Silver Nitrate.—Thirty grams to one liter + 0.4 Cc. HNO_3.

Sodium.

Sodium Chloride.—Ordinary "coarse fine" salt for freezing mixtures.

Sodium Hydrate.—36° Baumé. Dissolve three hundred grams of caustic soda in one liter of water.

Sodium Nitroprusside.—The commercial salt.

Sodium Thiosulphate.—$\frac{N}{10}$: Dissolve twenty-six grams of "sodium hyposulphite" in one liter of water; the addition of two grams of ammonium carbonate to the liter is said by Mohr to improve the stability of the solution.

Starch Solution.—Rub up in a mortar one gram of potato starch with ten to fifteen cubic centimeters of water, pour this into two hundred cubic centimeters of water which are boiling actively, and continue the boiling for a few minutes.

Sugar.—Ordinary granulated sugar.

Sulphur.—A 1.5 per cent. solution in carbon bisulphide.

Sulphuric Acid, C. P.—This should be at least ninety-nine and five-tenths per cent. pure, and its strength be determined by titration, as one hundred per cent. and ninety-four and three-tenths per cent. acid have the same specific gravity, 1.8384.[1]

Dilute.—One part acid to ten parts of water.

Nitrosulphuric Acid, for the Elaidin Test.—A liter of sulphuric acid of 46° Baumé (1.47 specific gravity) is prepared by diluting five hundred and sixty cubic centimeters commercial sulphuric acid to one liter; a few drops of nitric acid are added and nitric oxide (generated from copper and nitric acid) passed in until it is saturated. The acid is then cooled in ice-water and the gas passed in until it is saturated at 0° C. This is called Roth's liquid.

Tin Tetrabromide.—This is prepared[2] by allowing bromine to fall drop by drop upon granulated tin contained in a dry flask im-

---

[1] Richmond, J. Soc. Chem. Ind., 9, 479 (1890).

[2] Allen, Commercial Organic Analysis, ii, 463.

mersed in cold water until the coloration shows bromine to be in excess. A small quantity of bromine is then added and the liquid diluted with three to four times its volume of carbon bisulphide.

OILS FOR RAILROAD USE.

The railroads being among the largest users of oil, their requirements are of interest; as they do not differ widely, those of the Philadelphia and Reading Railroad will serve as a sample.

Specifications for Lard Oil.

When a shipment of oil is received a sample will be taken at random from each sixty barrels or fraction thereof, and forwarded to the Test Department. This sample will be examined and the entire shipment accepted or rejected on its merits. If rejected the shipment will be returned at the shipper's expense.

Two grades of Lard Oil will be used, "Prime" and "Extra No. 1"; the former for burning purposes chiefly, and the latter as a lubricant. The material desired under this specification is oil from fresh lard of corn-fed hogs, unmixed with other oils. It should contain the least possible amount of free acid, and from October 1 to May 1 show a cold test not higher than 40° F.

Prime Lard Oil.

This grade of oil must not contain admixtures of any other oils or more free acid than is neutralized by three cubic centimeters of alkali, as described below.

Between October 1 and May 1 it must show a cold test below 45° F.

When tested with nitrate of silver, as described below, it must not show any coloration.

Extra No. 1 Lard Oil.

This grade of oil must not contain admixtures of any other oils or more free acid than is neutralized by six cubic centimeters of alkali, as described below.

Between October 1 and May 1 it must show a cold test below 45° F.

The Cold Test.—The cold test is made as follows:

About two ounces of oil are put in a four-ounce sample bottle, a thermometer inserted, and the oil frozen with ice, salt being used if necessary. When the oil is hard, the bottle is taken from the freezing mixture and the frozen oil stirred thoroughly with the thermometer until it will flow. The reading of the thermometer is then taken, and this temperature is regarded as the cold test of the oil.

Free Acid Test.—The solutions required for this test are ninety-five per cent. alcohol neutralized with sodium carbonate, caustic potash solution of such a strength that 31.5 cubic centimeters of it will exactly neutralize five cubic centimeters of a normal solution of sulphuric acid (forty-nine grams per liter), and a small amount of Phenolphthalein dissolved in Alcohol, and rendered neutral with caustic potash, to be used as an indicator.

Now weigh or measure into a four-ounce sample bottle 8.9 grams of the oil to be tested, add about two ounces of Alcohol, warm to about 150° F., and add a few drops of the Phenolphthalein.

Then run in the caustic potash from a graduated burette, with frequent shaking, until a permanent pink color remains after vigorous shaking. When this point is reached read the number of cubic centimeters used.

Nitrate of Silver Test.—Solution of Nitrate of Silver is made as follows:

Nitrate of Silver, 1 gram; Alcohol, 200 grams; Ether, 40 grams. After the ingredients are dissolved and mixed, allow the solution to stand in a bright light until it has become perfectly clear; it is then ready for use, and should be kept in a dim place, and tightly corked.

Into a fifty cubic centimeter test-tube put ten cubic centimeters of the oil to be tested, previously filtered through washed filter-paper. Add five cubic centimeters of the above solution, shake thoroughly, and heat in a vessel of boiling water fifteen minutes with occasional shaking. If the oil is satisfactory it will show no change of color under this test.

Specifications for Petroleum Products.

When a shipment of oil is received, a sample shall be taken at random and forwarded to the Test Department. This sample will be examined and the entire shipment accepted or rejected on its merits. If rejected, the shipment will be returned at the shipper's expense.

150° Fire Test Oil.

This grade of oil shall be water-white in color, showing a flashing point not below 130° F., and a burning point not below 151°. The test will be made in an open vessel by heating the oil not less than ten degrees per minute, and applying the test flame every seven degrees, beginning at 123°. The gravity may be from 46° to 50° Baumé. Oil will not be received which is cloudy from the presence of glue or suspended matter of any kind.

300° Fire Test Oil.

This grade of oil shall be water-white in color, show a flashing point not below 256° F., and a burning point not below 298°. The test will be made in an open vessel by heating the oil not less than fifteen degrees per minute, and applying the test flame every seven degrees, beginning at 249°.

When heated to a temperature of 425° and held there for five minutes, the oil must remain clear and transparent, showing but a slight darkening and no separation of flocculent or other matter,—either at this temperature or on cooling.

When the oil is cooled to the temperature of 32°, and held there for ten minutes, it must remain clear and transparent, showing no cloudiness. The gravity may be from 38° to 42° Baumé.

Oil will not be received which is cloudy from the presence of glue or suspended matter of any kind.

Car Oil.

This grade of oil, commonly known as Well Oil or Black Oil, should have a gravity of about 29° Baumé, and must not show a flashing point below 325° F. The test will be made in an open vessel by heating the oil not less than fifteen degrees per minute, and applying the test flame once in seven degrees, beginning at 304°.

Oil received during the months of August and September must have a cold test not above 15° F., and from October 1 to April 1, a cold test not above 5° F. when determined as described below.

From August 1 to April 1, at 80° F., the oil must show a viscosity not lower than that of a pure cane sugar solution containing eighty grams of sugar in one hundred cubic centimeters of the syrup, and at 150° F. a viscosity not lower than that of a pure cane sugar solution containing sixty-six grams of sugar in one hundred cubic centimeters of the syrup, the viscosity of the sugar solution being taken at 80° F.

From April 1 to August 1, at 80° F., the oil must show a viscosity not lower than that of a pure cane sugar solution containing eighty-eight grams of sugar in one hundred cubic centimeters of the syrup, and at 150° F. a viscosity not lower than that of a pure cane sugar solution containing sixty-eight grams of sugar in one hundred cubic centimeters of the syrup, nor higher than that given by a pure cane sugar solution containing seventy-five grams of sugar in one hundred cubic centimeters of the syrup, the viscosity of the sugar solutions being taken at 80° F.

The oil must be transparent with a reddish-brown or greenish color, free from lumps or specks.

No oil will be accepted which shows more than five per cent. of flocculent or tarry matter settled out after five cubic centimeters of the oil have been mixed with ninety-five cubic centimeters of 88° Gasolene, and allowed to stand for an hour.

CYLINDER STOCK.

This grade of oil shall show a flashing point not below 525° F., and a burning point not below 600° F. The test will be made in an open vessel by heating the oil not less than twenty degrees per minute, and applying the test flame every seven degrees, beginning at 504°.

This oil must flow readily at 60° F., and at 350° F. must show a viscosity not lower than that of a pure cane sugar solution containing fifty-eight grams of sugar in one hundred cubic centimeters of the syrup, the viscosity of the sugar solution being taken at 80° F.

The oil must be transparent, with a reddish-brown or greenish color, free from lumps or specks.

No oil will be accepted which shows more than five per cent. of flocculent or tarry matter settled out after five cubic centimeters of the oil have been mixed with ninety-five cubic centimeters of 88° Gasolene, and allowed to stand for one hour.

Cold Test.—About two ounces of oil are put in a four-ounce sample bottle, a thermometer inserted, and the oil frozen with a mixture of ice and salt. When the oil is hard the bottle is taken from the freezing mixture and the frozen oil stirred thoroughly with the thermometer until it will flow. The reading of the thermometer is then taken, and this temperature is regarded as the cold test of the oil.

NOTE.—The viscosity tests will be made upon the Torsion Viscosimeter.

Manufacturers not having this instrument may submit a sample of oil to the Test Department, and will be furnished with the information necessary to standardize the viscosimeter they may have in use.

Specifications for Compound Oils.

When a shipment of oil is received, a sample shall be taken at random and forwarded to the Test Department. This sample will be examined and the entire shipment accepted or rejected on its merits. If rejected, the shipment will be returned at the shipper's expense.

CYLINDER OIL.

This oil shall consist of a high-grade cylinder stock, compounded with not less than twenty per cent. by weight of acidless animal oil, Tallow or Tallow Oil being preferred.

The compounded oil shall show a flashing point not below 525° F., and a burning point not below 600°. The test will be made in an open vessel by heating the oil not less than twenty degrees per minute, and applying the test flame every seven degrees, beginning at 504°.

This oil must flow readily at 60° F., and at a temperature of 350° F. must show a viscosity not lower than that of a pure cane sugar solution containing fifty-eight grams of sugar in one hundred cubic centimeters of the syrup, the viscosity of the sugar solution being taken at 80° F.

The oil must be transparent, with a reddish-brown or greenish color, free from lumps or specks.

No oil will be accepted which shows more than five per cent. of flocculent or tarry matter settled out after five cubic centimeters of the oil have been mixed with ninety-five cubic centimeters of 88° Gasolene, and allowed to stand for one hour.

SIGNAL OIL.

This grade of oil shall be prime white in color, shall contain not less than forty per cent. by weight of Prime Lard Oil, and shall show a flashing point not below 200° F., and a burning point not above 300°. The test will be made in an open vessel by heating the oil not less than fifteen degrees per minute, and applying the test flame every seven degrees, beginning at 193°.

When heated to a temperature of 450°, and held there for five minutes, the oil must remain clear and transparent, showing but a slight darkening and no separation of flocculent or other matter, either at this temperature or on cooling. The gravity may be from 31° to 34° Baumé.

Oil will not be received which is cloudy from the presence of glue or suspended matter of any kind.

No. 1 Engine Oil.

This oil shall consist of a high grade of mineral oil, compounded with not less than ten per cent. by weight of nearly acidless animal oil.

It shall show a gravity of about 29° Baumé, and a flashing point not below 325° F. The test will be made in an open vessel by heating the oil not less than fifteen degrees per minute, and applying the test flame once in seven degrees, beginning at 304°.

Oil received during the months of August and September must have a cold test not above 15° F., and from October 1 to April 1 a cold test not above 5° F., when determined as described below.

From August 1 to April 1, at 80° F., the oil must show a viscosity not lower than that of a pure cane sugar solution containing eighty grams of sugar in one hundred cubic centimeters of the syrup, and at 150° a viscosity not lower than that of a pure cane sugar solution containing sixty-six grams of sugar in one hundred cubic centimeters of the syrup, the viscosity of the sugar solution being taken at 80° F.

From April 1 to August 1, at 80° F., the oil must show a viscosity not lower than that of a pure cane sugar solution containing eighty-eight grams of sugar in one hundred cubic centimeters of the syrup, and at 150° F. a viscosity not lower than that of a pure cane sugar solution containing sixty-eight grams of sugar in one hundred cubic centimeters of the syrup, nor higher than that given by a solution of pure cane sugar containing seventy-five grams of sugar in one hundred cubic centimeters of the syrup, the viscosity of the sugar solutions being taken at 80° F.

The oil must be transparent, with a reddish-brown or greenish color, free from lumps or specks.

No oil will be accepted which shows more than five per cent. of flocculent or tarry residue settled out after five cubic centimeters of the oil have been mixed with ninety-five cubic centimeters of 88° Gasolene, and allowed to stand for an hour.

No. 2 Engine Oil.

The requirements for this oil are identically the same as those for No. 1 Engine Oil, with the following exceptions:

It must contain not less than twenty per cent. by weight of nearly acidless animal oil.

From October 1 to April 1 the cold test must be not above 10° F. when determined as described below.

Screw-Cutting Oil.

This oil shall consist of paraffine oil of about 27° Baumé gravity, compounded with not less than twenty-five per cent. by weight of Fat Oil, Cotton-seed preferred.

The compound oil shall show a flashing point not below 300° F., and a burning point not above 425°. The test will be made in an open vessel by heating the oil not less than fifteen degrees per minute, and applying the test flame once in seven degrees, beginning at 276°.

From October 1 to April 1 the oil must have a cold test not above 15° F. when determined as described below.

Cold Test.—About two ounces of oil are placed in a four-ounce sample bottle, a thermometer inserted, and the oil frozen with a mixture of ice and salt. When the oil is hard, the bottle is taken from the freezing mixture, and the frozen oil stirred thoroughly with the thermometer until it will flow. The reading of the thermometer is then taken, and this temperature is regarded as the cold test of the oil.

Note.—The viscosity tests will be made upon the Torsion Viscosimeter.

Manufacturers not having this instrument may submit a sample of oil to the Test Department, and will be furnished with the information necessary to standardize the instrument they may have in use.

Specifications for Tallow.

Tallow to be used for cylinder lubrication should be rendered as soon as possible after the animal is killed, in order to have the amount of free acid as small as possible.

Tallow which on examination is found to contain dirt or cracklings disseminated through it, or which has a layer of dirt or cracklings in the bottom of the barrel more than an eighth of an inch thick, will be rejected.

Tallow will not be accepted which has more free acid than can be neutralized by three cubic centimeters of the alkali solution used for this determination (p. 177), or which contains any foreign substance not properly belonging to tallow.

Specifications for Motor Gasoline.

(As adopted by the Committee on Standardization of Petroleum Specifications, November 25, 1919.)

Inspection and Tests. Samples are taken at random and retained in a clean, tight vessel.

Test.—100 cc. are distilled according to Technical Paper No. 214 (p. 210). This uses an Engler flask and ice-water cooled condenser.

(*a*) Boiling point must not be higher than 60 C°.

(*b*) Twenty per cent. must distil below 105°.

(*c*) Fifty per cent. must distil below 140°.

(*d*) Ninety per cent. must distil below 190°.

(*e*) End point of distillation must not be higher than 225°.

(*f*) Not less than 95 per cent. of the liquid must be recovered from the distillation.

The Improved MacMichæl Viscosimeter.

As originally introduced the range was limited from the viscosities of the light liquids to that of pure glycerine. Many important improvements have been made in the new MacMichæl and the instrument,[1] as now supplied, is adapted for the accurate determination not only of the lighter liquids, as formerly, but also for very viscous substances, as, for example, the heaviest and stiffest glues.

A bob, either disc *e* or cylinder *f* is suspended in a cup, *c* or *d*, by means of a torsion wire about ten inches long running down through the stem of the spindle *g* and fastened near the bottom. Both bobs are provided with bayonet locking devices so that they may be quickly attached to the spindle. The head of the torsion wire is triangular and is held between two grooved pins *l* attached to a circular revolving head *m*. This head is divided into 30 equal sections, and can be set in as many different positions, each section corresponding to 10° on the graduated dial *i*. The head is used only when making readings to tenths of a degree, with the aid of a reflecting mirror cath-

---

[1] See also Herschel, J. Ind. & Eng. Ch. 12, 282 (1920).

etometer, a small mirror being attached to the spindle for this purpose. Dial *i*, which is divided into 300 equal parts, is secured at the top of the plunger by means of a friction disc, permitting the adjustment of the zero mark to its proper location. A pointer *k* is set by the operator to the zero point on the dial before making the test. The final point of rest of the dial is indicated by the pointer and can be read to half a subdivision. A dash pot *h* is attached to the spindle to stabilize the motion. The cup *c* is placed in an outer cup *b*, which serves as an oil jacket. The oil can be heated by means of an electric heater in the bottom of *b*. *C* is provided with an opening for a thermometer and a cover *x* is used to prevent heat radiation. Cup *d*, which is intended for use with bob *f*, is inserted in cup *c*, oil being placed in the latter if the material is to be heated. For ordinary purposes with the lighter liquids bob *e* is usually employed; for more viscous materials bob *f* is used. This bob is concave at the bottom and has a diameter of 1 cm. while cup *d* is 3 cm. inside diameter, giving a clearance around the bob of 1 cm. By regulating the speed to the rate of 1 cm. per second, the force in dynes required to move 1 sq. cm. of the substance under test past another sq. cm., 1 cm. apart, can be computed.

All of the cups are locked by means of slots and pins, the oil cup being fastened to the rotating platform *a*. This platform is revolved at a uniform rate of speed by means of a motor drive. The motor *p* can be run at two different speeds by means of gearing *q*. It is equipped with a governor *r* so that any speed from about 6 to 120 R. P. M. can be obtained. Motor and governor are enclosed in dust proof case *v*. The base and the upright *n* are strongly constructed and leveling screws are provided to secure an accurate vertical position. A handle *o* is attached to the upright so that the instrument can be readily carried. The ordinary lighting circuit can be used for operation and heating. Switch *t* is for starting the motor. The plugs *u*, attached to leads, are used for connecting the current with the oil cup. The leads are provided with a switch *u*, which should be off when attaching the plugs to pins on cup *b*, to avoid arcing.

The operation of the instrument is described on page 34.

Specifications for Testing Motor Gasoline.[1]

One hundred cubic centimeters are distilled in an Engler flask provided with a metal condenser and special thermometer. These are described as follows:

---

[1] Bureau of Mines Technical Paper, 214.

FLASK

The flask used shall be the standard 100 cc. Engler flask, described in the various textbooks on petroleum. Dimensions (outside) are as follows:

DIMENSIONS OF FLASK.

Dimensions	cm.	inches
Diameter of bulb	6.5	2.56
Diameter of neck	1.6	0.63
Length of neck	15.0	5.91
Length of vapor tube	10.0	3.94
Diameter of vapor tube	0.6	0.24

Position of vapor tube, 9 cm. (3.55 inches) above the surface of the gasoline when the flask contains its charge of 100 cc. The tube is approximately in the middle of the neck.

The flask shall be supported on a ring of asbestos having a circular opening 3 cm. (1¼ in.) in diameter; this means that only this limited portion of the flask is to be heated. The use of wire gauze or a sand bath is not approved.

CONDENSER.

The condenser shall consist of a thin walled tube of metal (brass or copper), approximately 13 mm. (0.5 in.) internal diameter and 55 cm. (22 in.) long. It shall be set at an angle of 75° from the perpendicular, and shall be surrounded with a cooling jacket of the trough type. The lower end of the condenser shall be cut off at an acute angle and shall be curved down for a length of 7.5 cm. (3 in.). The condenser jacket shall be 15 in. long.

SPECIFICATIONS FOR GASOLINE DISTILLATION THERMOMETER.

The thermometer should be made of selected enamel-backed tubing having a diameter between 5.5 and 7 mm. The bulb should be of Jena normal or Corning normal glass; its diameter should be less than that of the stem and its length between 10 and 15 mm. The total length of the thermometer should be approximately 380 mm. The range should cover 0° C. to 270° C., with the length of the graduated portion between the limits of 210 to 250 mm. The point marking a temperature of 35° C. should be not less than 100 mm. nor more than 120 mm. from the top of the bulb.

The scale should be graduated for total immersion. The accuracy must be within about 0.5° C. The space above the meniscus must be filled with an inert gas, such as nitrogen, and the stem and bulb must be thoroughly aged and annealed before being graduated.

All material and workmanship must be of the best. The scale shall be marked for single-degree intervals. Each tenth degree shall be numbered, and each fifth degree distinguished by a longer mark.

Source of Heat in Gasoline Distillation.

The source of heat in distilling gasoline may be a gas burner, an alcohol lamp, or an electric heater. The commonly used Tirrell type of gas burner is moderately satisfactory, but a burner having a smaller orifice and a more sensitive regulating valve is more desirable. For the bulk of its own work the bureau of mines has used specially designed and constructed electric heaters which have proved considerably more satisfactory then either gas or alcohol burners.

Electric heaters are superior to the other types in that they permit more exact regulation of the degree of heat, are not subject to serious uncontrollable fluctuation (such as is caused by air currents) and involve a minimum danger of fire.

MANIPULATION.

1. If an electric heater is used it is started first to warm it.

2. The condenser box is filled with water containing a liberal proportion of cracked ice.

3. The charge of gasoline is measured into the Engler flask from a 100 cc. graduate. This graduate is used as a receiver for distillates without any drying. This procedure eliminates errors due to incorrect scaling of graduates and also avoids the creation of an apparent distillation loss due to the impossibility of draining the gasoline entirely from the graduate.

4. The graduate is placed under the lower end of the condenser tube so that the latter extends downward below the top of the graduate at least 1 in. The condenser tube should be so shaped and bent that the tip can touch the wall of the graduate on the side adjacent to the condenser box. This detail permits distillates to run down the side of the graduate and avoids disturbance of the meniscus caused by the falling of drops. The graduate is moved occasionally to permit the operator to ascertain that the speed of distillation is right, as indicated by the rate at which drops fall. The proper rate is from 4 cc. to 5 cc. per minute which is approximately two drops a second. The top of the graduate is covered, preferably by several thicknesses of

filter paper, the condenser tube passing through a snugly fitting opening. This minimizes evaporation losses due to circulation of air through the graduate and also excludes any water that may drip down the outside of the condenser tube on account of condensation on the ice-cooled condenser box.

5. A boiling stone (a bit of unglazed porcelain or other porous material) is dropped into the gasoline in the Engler flask. The thermometer, equipped with a well-fitted cork and with its bulb covered with a thin film 5-10 mg. of absorbent cotton (preferably the long-fibered variety sold for surgical dressings), is fitted into the flask with the thermometer bulb just below the lower level of the side neck opening. The flask is connected with the condenser tube.

6. Heat is applied cautiously and the gasoline brought to its boiling point. In case it is desired to record the initial boiling point the thermometer is read when the first drop falls from the end of the condenser tube into the graduate. The amount of heat is then increased so that the distillation proceeds at a rate of from 4 cc. to 5 cc. per minute. The thermometer is read as each of the selected percentage marks is reached. In case maximum boiling point or dry point (one definition of end point) is to be measured, the heating is continued after the flask bottom has boiled dry until the column of mercury reaches a maximum and then starts to recede consistently.

7. Distillation loss is determined as follows: The condenser tube is allowed to drain for at least five minutes after heat is shut off, and a final reading taken of the quantity of distillate collected in the receiving graduate. The distillation flask is removed from the condenser and thoroughly cooled as soon as it can be handled. This can be accomplished by using first an air bath and then immersing the bulb of the flask in the ice-water mixture in the condenser trough. The condensed residue is poured into a small graduate or graduated test tube and its volume measured. This residue is retained for the acidity test, p. 21. Test the distilled water for acid. The sum of its volume and the volume collected in the receiving graduate, subtracted from 100 cc. gives the figure for distillation loss. In case this loss exceeds 2 per cent., a check distillation should be run to ascertain whether such loss is due to the presence of highly volatile constituents or to failure to condense the lighter fractions on account of too strong heating at the beginning of the distillation.

Some of the prescribed details of procedure merit discussion. The use of a boiling stone is desirable to prevent "bumping," which occasionally occurs, especially when the Engler flask is new or freshly cleaned. The film of cotton on the thermometer bulb retains a layer of condensed gasoline and insures against superheating, either in the course of the distillation or at the end point. Superheating manifests itself as an irregular fluctuation of the thermometer during distillation, or as an abnormal rise at the end. The film of cotton should be very thin and in case of doubt the quantity used (5 to 10 mgs.) should be weighed.

Avoidance of an excessive distillation loss is important, as otherwise the temperature readings will be abnormally high. If blends containing considerable proportions of casing-head gasoline are distilled, it may be necessary to use an ice-salt freezing mixture in the condenser trough and to keep the receiving graduate immersed in a mixture of ice and water (preferably not the ice-salt freezing mixture). If this is done the gasoline must be cooled in ice and water before measuring it into the flask, or else a suitable allowance (approximately 3 per cent.) must be made for the contraction of the gasoline due to cooling it from room temperature to the freezing point of water.

Automobile Oils.[1]

The Specifications of the U. S. War Dept. are as follows:

Saybolt Universal	Light	Medium	Heavy
Visc. 100° F.	175–210	275–310	370–410
Visc. 210° F.	40–47	45–54	55–68
[2] Flash ° F.	325	335	345
Fire ° F.	365	380	390
Conradson's [3] Carbon residue %	0.2	0.3	0.4

Acidity. Not more than 0.05 mg. KOH per gram oil.

Late Analytical Methods and Specifications.

Inasmuch as specifications for oils, and their methods of analysis are now being widely and intently studied—they are in a state of change. Those seeming] best adapted or most authoritative are here given to be transferred to the body of the book when generally accepted.

---

[1] Battle, p. 1056.

[2] Cleveland Cup.

[3] According to A.S.T.M. methods.

Bailey and Baldsiefen's Hexabromide Method.

REAGENTS.

The following reagents in about the quantities mentioned will be required for making ten determinations:

Sodium Hydroxide Solution.—(1.4 sp. gr.)—Dissolve 75 g. of C. P. NaOH in water and make up to 200 cc.

Alcohol.—(95 per cent. by volume).—200 cc. (denatured alcohol is satisfactory).

Hydrochloric Acid.—C. P., concentrated 300 cc.

Glacial Acetic Acid.—20 cc. This acid should show no reduction in the usual bichromate or permanganate tests.

Glacial Acetic Acid Solution of Bromine.—30 cc. Five cc. of bromine + 25 cc. of acetic acid. The bromine must be free from non-volatile matter.

Ether Saturated at 0° C. with Linseed Oil Hexabromides.—Wash in a separatory funnel a liter of U. S. P. ethyl ether with four successive 100-cc. portions of distilled water (ice-cold) and dry with fused calcium chloride over night. In the morning, pour the ether off through a folded filter paper into a 1.5—or 2-liter flask. Add several thin slices of sodium, reflux until there is no longer any evidence of the liberation of hydrogen, then distil off the dry ether.

Before the ether can be used it must be saturated at 0° C. with the hexabromides of linseed oil fatty acids to prevent its dissolving hexabromides during the washing of the bromination products in the determination. To prepare the hexabromides for this purpose, the directions given below have been found very satisfactory.

In a centrifuge tube dissolve about 5 g. of the fatty acids in 25 cc. of ether. Place the tube in a freezing mixture and add slowly, with shaking, bromine solution, until a red color is permanent. Let stand for at least 15 min., whirl the tube in a centrifuge until the precipitate has settled, and then pour off the ether. Rub up the precipitate with 20 cc. of cold absolute ether, whirl in a centrifuge, and pour off the wash ether. Repeat the washing with three more 20-cc. portions of ether. After drying, the hexabromide so obtained is pure enough for the preparation of the wash ether.

To saturate the dry ether with the hexabromides thus prepared, or those from previous determinations made of pure linseed oils, which should always be saved, add at least 3 g. of the finely powdered

---

[1] From J. I. & Eng. Chem. 12, 1189 (1920).

substance and allow the solution to stand at room temperature with frequent shaking for several hours. Cool in ice water for 2 hrs., shaking from time to time, and finally filter as rapidly as possible into a dry cork-stoppered bottle.

APPARATUS.—In addition to the ordinary equipment of a chemical laboratory, it is essential for the proper handling of this method to have the following apparatus:

(a) Twelve centrifuge tubes about 1x5 inches of well-annealed heavy glass.

(b) A laboratory centrifuge with cups for holding the above centrifuge tubes.

DETERMINATION.—*Preparation of the Fatty Acids.*—To 50 cc. of oil in a 2-liter, round-bottom flask, add 40 cc. of the NaOH solution and 40 cc. of alcohol. Close the flask with a 2-hole rubber stopper, carrying a quarter-inch tube, the lower end of which is just above the surface of the liquid, and heat on the steam bath for about 0.5 hr. Add a liter of hot distilled water and boil the soap solution until the alcohol is removed, passing a stream of CO_2 continually through the inlet tube. If a free flame is used, about 0.5 hr. boiling will be sufficient, but in this case it may be necessary to insert capillary tubes to prevent bumping of the liquid. If the solution is heated on the steam bath, 2 to 3 hrs. are usually required. After removing the alcohol, cool slightly, acidify with dilute HCl (1:1) and warm until the fatty acids form a clear layer (continuing to pass CO_2 through the system all the time). Transfer the fatty acids and part of the solution to a 500-cc. separatory funnel, allow to stand a few minutes until the fatty acids collect on top of the aqueous portion, and draw this off. Pour the remainder of the mixture from the flask into the funnel, and run off the aqueous portion. Add 300 cc. of hot water, shake vigorously, allow the fatty acids to separate, and again draw off the aqueous portion. Repeat this process until the wash water is neutral to methyl orange, three washings usually being sufficient. Run the warm fatty acids at once into a centrifuge tube and whirl for about a minute to separate the remaining water, then filter through a folded filter paper into a small bottle. When the major portion of the acids have run through the filter, discard the remainder, and stopper the bottle with a tight cork. It is obvious that the acids must be hot enough when poured on the filter to remain completely liquid until filtered, as otherwise some of those with a high melting point may separate.

Precipitation of the Hexabromides.—Weigh accurately one of the centrifuge tubes, pipet into it as nearly as practicable 1.00 g. of the prepared fatty acids and again weigh. For transferring the fatty acid, a piece of 5 mm. glass tubing about 20 cm. long, drawn out to a tip and bent down at the lower end and up at the other in a shape similar to a "S" wrench, is convenient. To the fatty acids in the centrifuge tube add 25 cc. of the ether saturated with hexabromides and 2 cc. of glacial acetic acid. Cool the tube and its contents to about— 10° C. by immersion in a bath of chopped ice to which a little commercial hydrochloric acid has been added; then, keeping the tube in the cooling mixture, add from a burette the bromine reagent at the rate of one or two drops per second, shaking the tube after each addition. Continue the bromination until the solution of fatty acids becomes permanently orange in color (usually for pure linseed oil this requires about 2.5 cc.), then remove the tube from the bath, stopper it with a cork, and allow to stand over night in an ice box.

Washing and Weighing of the Hexabromides.—Next morning cool the tube by immersion in a bath of cracked ice and rub up the precipitate by means of a weighed glass rod, being sure to loosen any material adhering to the side of the tube. Whirl the tube in a centrifuge till the precipitate forms a hard cake on the bottom, cool in the ice bath, and decant the ether. Add 20 cc. of the wash ether previously cooled to 0° C. and rub up the precipitate with the glass rod. Return the tube to the ice bath and when cool remove and whirl again in the centrifuge. Cool once more and then remove the ether by decantation. Repeat this washing twice more, and after the last washing incline the tube and carefully tap it to spread the hexabromide precipitate part way up the sides. Warm the tube in water at 60° C. until most of the ether has evaporated, then attach it for 15 min. to a vacuum line showing a pressure of 30 to 40 mm., keeping the temperature around 60° C. Wipe the tube dry and allow it to stand in the balance at least 15 min. before weighing. To the weight of the precipitate in the tube add the weight of the slight amount adhering to the glass rod. This total weight of precipitate, multiplied by 100 and divided by the weight of the fatty acids taken, gives the hexabromide percentage.

The table below shows the results obtained:

	Results Per cent.
Linseed oil	41.1 — 44
Linseed oil boiled	41.9 — 42.6
Linseed oil heavy bodied	— 10
Menhaden	35.9 — 36.2
Soy bean	4.3 — 7.5
China wood	0.0 —

INDEX